

**AFML-TR-74-135**

**Part I**

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**DEVELOPMENT OF HIGHLY ORIENTED POLYMERS  
WITH IMPROVED MECHANICAL PROPERTIES**

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*INSTITUTE OF POLYMER SCIENCE  
THE UNIVERSITY OF AKRON*

**TECHNICAL REPORT AFML-TR-74-135**

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13. ABSTRACT <p>The basic need for stronger polymeric films is discussed in the context of new theoretical and experimental evidence. It is shown that extended-chain crystals of polymers, that is, polymer chains which do not fold back on themselves should have high strength and stiffness. However, it is necessary to utilize these materials in the form of films that have <u>all</u> of the chains oriented in <u>one</u> direction. It is shown that such laminates should and do have enhanced mechanical properties.</p> <p>Experiments to produce such oriented films with polyethylene crystallized in a shear field are reported. Although there is chain orientation and enhanced mechanical properties, the films lack integrity and tend to pull apart easily in the direction perpendicular to the chain axis. A stirred, high-pressure crystallizer was designed and assembled, although no data have yet been obtained. Screening tests to evaluate a variety of materials were conducted with several polymers. Poly(n-alkyl isocyanates) were cast as ultra-thin films and show promise as a high regular extended-chain crystal. Preliminary X-ray diffraction studies of these materials was carried out for future use on materials crystallized in the high-pressure, stirred crystallizer.</p>			

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## 1. PREPARATION OF HIGHLY ORIENTED POLYMERIC MATERIALS

### 1.1. Introduction

It is possible to obtain significant increases in strength and stiffness values for polymers if the chains are fully extended so that their deformation is not governed any more by conformational changes due to bond rotation. The load applied to a fully extended chain will then be supported by the primary bonds and the extension of the chain will be very small since it will result only from the bending of these (normally  $110^\circ$ ) bonds. Large stiffness and strength values can therefore be expected.

### 1.2 Theoretical and Experimental Stiffnesses of Extended Chains

The stiffnesses of extended chains have been determined experimentally as well as theoretically. Since it has not been possible to date to produce polymeric solids with fully extended chains (with the possible exception of fibers, as discussed later) the stiffness values have been measured on drawn crystalline polymers<sup>1</sup>. The lattice strains were measured by an X-ray technique in the direction of the fiber axis as well as that perpendicular to it. The moduli for both directions were calculated on the assumption that the stress is

homogeneous within a specimen under load. Results were obtained for various kinds of polymers and were explained in terms of the crystalline structure of the polymers, particularly the skeleton conformation and the cross-sectional bulkiness of the chain. The moduli in the direction of the fiber axis are significantly different depending upon the polymer.

Some of these values are listed in Table I and are compared with typical properties of conventional composites. As can be seen readily, the stiffness values of these ideally oriented chains compare very favorably with those of the stiffest composite and in some cases even exceed them.

Polyethylene<sup>2</sup> and poly(vinyl alcohol)<sup>3,4</sup> in the crystalline (or fully extended) state assume a fully extended planar zigzag conformation of the carbon chain as shown in Fig. 1a. and have therefore high  $E_{11}$  values. The extension of the

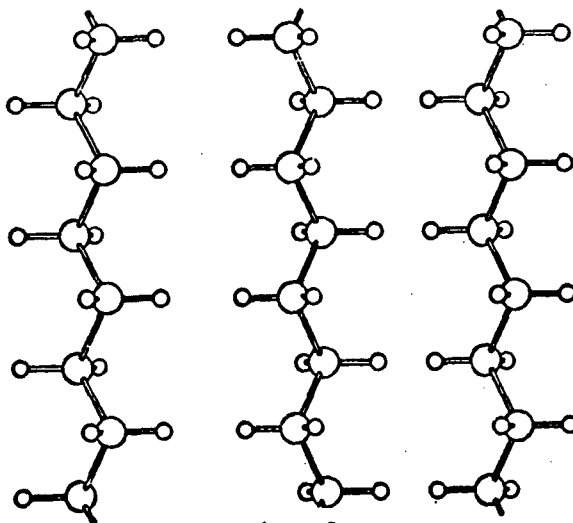
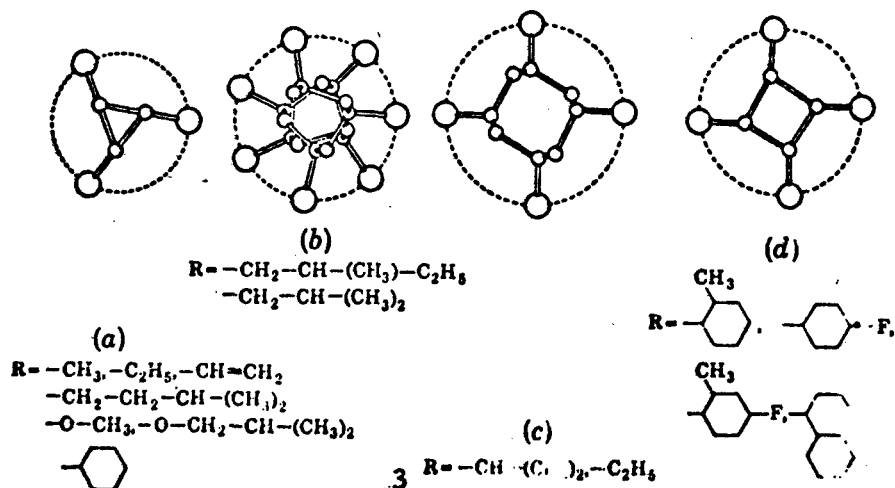
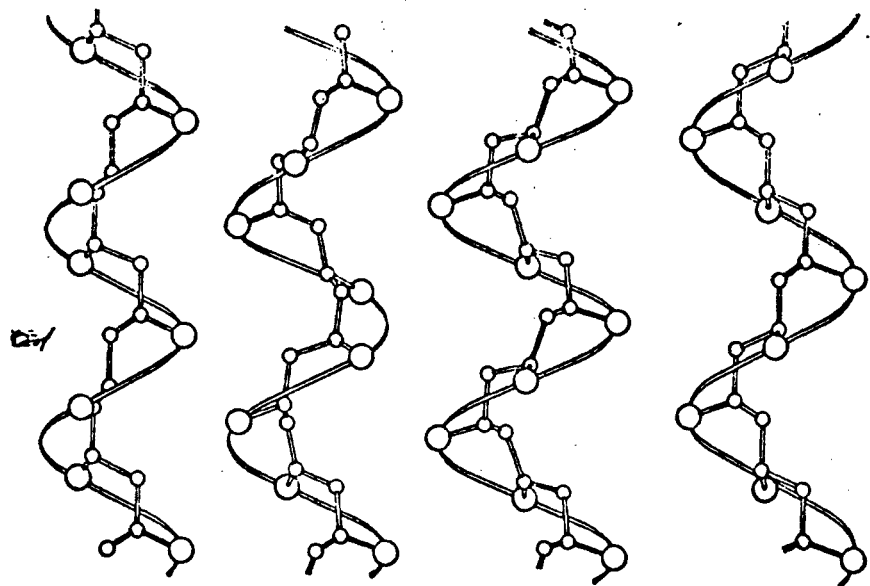


Fig. 1a

Fully extended Planar Zigzag Conformation  
of the Carbon Chain

chain occurs in this case by bond stretching and deformations of the bond angle. Many calculations on the elastic modulus of such a fully extended paraffin chain have been published and only the three most recent ones shall be mentioned: 26.4 psi<sup>5</sup>, 49.0 psi<sup>6</sup>, 20.9 psi<sup>7</sup>. The observed value shows fairly good agreement with these calculated ones.

Polytetrafluoroethylene (PTFE), polypropylene (PP) and polyoxymethylene (POM) all assume a helical conformation of the chain in the fully extended state (see Fig. 1b). Their fiber



identity periods are contracted from those of the fully extended structures and the chain is more bulky, particularly if it has bulky side groups. The extension of the chain in these polymers involves simultaneous free rotations about the single bonds of the chains in addition to the mechanisms mentioned above for the fully extended structure. For this reason the  $E_{11}$  values are much smaller just as a helical steel spring is softer than an extended wire.

The value of the observed modulus of PTFE compares favorably with the calculated value<sup>6</sup>, as does that of POM<sup>7,8,9</sup>.

The relatively good agreement between the experimental and calculated values of the modulus suggest that sheets of fully extended polymer chains should exhibit stiffnesses comparable to those of high performance composites or metals.

Further evidence is supplied by the newly developed DuPont Fiber PRD-49 (Kevlar 49). The modulus values of three types of this fiber are also listed in Table I. Type I fiber values are comparable to those of PVA and PE. Even though the production procedure and the nature of the material are not exactly known at this time it can be safely assumed that these fibers consist of nearly fully extended polymeric chains.

If the techniques for the production of such fully oriented structures in the form of films are developed they would be suitable materials for the production of multiangular laminates, and could probably compete with conventional composites containing fibers. It is also conceivable that some other interesting and useful properties might make them superior products for certain applications.

### 1.3 Properties of Isotropic Laminates

The properties of isotropic laminates fabricated from this type of extended chain structure sheets have been calculated and compared with conventional fiber composites. The previously developed laminate theory<sup>10-14</sup> has been employed (see schematic in Fig.1c ). In particular the approximate relations for the moduli of an in-plane isotropic laminate are derived.

$$\tilde{E} = 3/8 E_{11} + 5/8 E_{22}; \quad \tilde{G} = 1/8 G_{11} + 1/4 E_{22}$$

The calculated values are listed in Table II. It can be readily seen that the stiffness of the PE and PVA laminate exceeds that of a Boron-Epoxy composite and that nearly all others are superior to the glass-Epoxy system.

These data indicate that a multi-layer isotropic composite of highly oriented polymeric material would be a

superior engineering material. These figures indicate that the properties of the final product would warrant the exploration and development of the fabrication techniques of this type of material.

#### 1.4 Previous Attempts to Prepare Chain Extended Crystals

There are primarily two basic routes used to achieve extended chain crystals in polymers. Wunderlich and coworkers<sup>15</sup> have pursued bulk crystallizations of polyethylene under elevated temperatures and high pressures. However, these crystallizations require tremendous pressures (up to 100,000 psi) as the driving force reorganizing the polymer chains.

Stirrer-induced crystallizations have been investigated by several workers including recent work by Keller<sup>16</sup>. Dilute solutions (~2%) are stirred at various conditions to orient the chains and then to have them crystallize. The obvious advantage to this procedure is that dilute solutions allow less severe conditions to be imposed on the polymer. Instead, a mild shear rate is employed as the driving force. It should be pointed out that up to this point, only very small amounts of polymer crystals have been obtained. No films have been prepared.

Extended chain polymer crystals should be revealed by the following characteristics:

1. By observing a thin sample between crossed polaroids under the optical microscope, the absence of spherulitic random crystallization is an indication of some degree of orientation. Fig. 2a shows examples of spherulitic and a more oriented type of structure.

2. A more conclusive test for high degrees of orientation is provided by X-ray scattering patterns of the crystals. The typical scattering pattern of an oriented film should give patterns which are seen on Fig. 2b as opposed to a randomly oriented structure. One may use these techniques to monitor degrees of orientation in a given sample.

#### 1.5 Preparation of Highly Oriented Film

At the beginning of this project, attempts were made to modify the work of Keller to produce an uniaxially oriented film by stirrer-induced crystallization methods. The systems used heretofore were comprised of 8 blade propellers in a test tube and only long "whisker like" fibrils were produced. Shear conditions were crude and unknown. It was proposed therefore to use a refined system of coaxial stainless steel cylinders where the inner cylinder rotates at a given rpm.

The shear rate,  $\dot{\gamma}$ , at the wall of rotating inner cylinders may be easily calculated as follows:

$$\dot{\gamma} = \Omega \frac{R_2^2 + R_1^2}{R_2^2 - R_1^2}$$

where

$\Omega$  = angular velocity

$R_2$  = radius of outer cylinder

$R_1$  = radius of inner cylinder

Because of small heat losses, the temperature on the surface of the inner cylinder is  $\sim .5^\circ\text{C}$  lower than the outer cylinder and crystallization would thus take place on the rotating inner surface. A film would therefore be expected to form on the smooth surface of the inner cylinder. Heating was accomplished by a strip heater jacket surrounding the outer cylinder having a temperature control of  $\pm .1^\circ\text{C}$ . A schematic representation of this system is seen in Fig. 3. Since the radii of the outer and inner cylinders were 4.2 cm. and 3.7 cm. respectively, the shear rate is varied by the rpm or angular velocity.

Marlex 50 polyethylene (Phillips Petroleum) was chosen for the initial work because several other investigators have obtained extended chain crystals with this material. Because of its extreme linearity (no detectable branching) and its



flexible chain, Marlex will crystallize relatively easily. Also it is soluble in most organic solvents above  $100^{\circ}\text{C}$ . Polyethylene oxide (Union Carbide) was also considered because of its flexible chain characteristics and high crystallinity. Furthermore it has the advantage of being soluble in water and alcohols at room temperature.

It was not easy to decide upon the optimum operating conditions for the stirred-crystallization. Marlex solutions are not easily handled in very concentrated solutions, yet it is necessary to use concentrated solutions in order to obtain a thick enough film for mechanical measurements. Two per cent solution of Marlex in xylene finally was found to be the best compromise. A stirred-crystallization time of 72 hrs. was thought to be sufficient based on those experiments previously mentioned<sup>16</sup>. It was also known that the workable crystallization temperature range was  $97^{\circ}\text{C}$ - $102^{\circ}\text{C}$ <sup>16</sup>. Below  $97^{\circ}\text{C}$  the polyethylene crystallizes rapidly in a folded chain conformation and above  $102^{\circ}\text{C}$  the yield of polymer is very small. That is, only the high molecular weight component is crystallized so that the very thin films would be too thin to test. The

optimum shear rate, which is varied by changing the rpm in the apparatus (Fig. 3), also had to be determined. The effect of post crystallization treatments such as annealing and washing also had to be evaluated.

Tensile tests of the resulting films were made using samples cut parallel to the axis of shear (the axis of main orientation) and cut normal to the orientation axis. X-ray diffraction patterns of the resulting films were taken to determine the degree of orientation on the molecular level.

#### 1.51 Experimental Results

Using the experimental apparatus shown in Fig. 3, experiments were designed to find a temperature that would produce a strong film of good integrity. The conditions employed for these experiments were as follows:

Temperatures	- 96,98,100,102°C
Shear rate	- 700 sec <sup>-1</sup>
Solution Concentration	- 2% Marlex in xylene
Time	- 72 hrs.

After 72 hours of stirring the films were washed with clean xylene at the temperature of crystallization to divest the film of extraneous material of low molecular weight. The

films were peeled off the stirrer and vacuum dried for 24 hrs. The films obtained were white and of a fibrous texture. The film thickness was irregular, but was found to be on the order of .05 mm. Films obtained at 102°C were too thin to test.

Subsequently, samples were cut from the films parallel and normal to the orientation axis. The samples were placed in an Instron Table Model Tester and tested in tension to failure at a crosshead speed of .05 cm/min. The stress-strain diagrams obtained from this series of samples are seen in Figs. 4-8. The film appearing to have the best overall strength and integrity was PE 11474 crystallized at 100°C. Wide angle X-ray diffraction patterns of this film are seen in Fig. 9a. In addition, a scanning electron micrograph was taken of the surface of this film, and as seen in Fig. 9b it appears to consist of large bundles of fibrils with some striations transverse to the fiber axis.

Experiments were then designed to investigate the effect of shear rate. The following conditions were employed:

Temperature	-	100°C
Shear rate	-	500,700,900 sec <sup>-1</sup>
Concentration	-	2% Marlex in xylene
Time	-	72 hrs.

These films had the same appearance as previous ones and were given the same post crystallization treatments. Samples for testing were cut in the same manner as above and the identical Instron Test conditions were employed. The resulting stress-strain diagrams are seen in Fig. 10.

Additional post crystallization treatments of stress annealing and washing under stress were studied to determine if they improved the samples. A sample of polyethylene Marlex (PE 11173) was crystallized at  $90^{\circ}\text{C}$ ,  $550\text{ sec}^{-1}$ , 72 hrs. A 50 gram weight was clamped to one end of the film and film was then hung in an air oven at  $100^{\circ}\text{C}$  for 24 hours. Afterwards the sample was allowed to relax for 24 hours and then tested in tension using the previously mentioned procedure. The resulting stress-strain diagrams are seen in Fig. 11. The X-ray diffraction patterns are seen in Fig. 12. Additionally, a 25 gram weight was clamped to a sample of PE 11774 and crystallized in the same manner. However, the film was suspended in xylene at  $65^{\circ}\text{C}$  for 12 hrs. The sample was vacuum dried for 24 hours unstressed and tested as before in tension. The results are seen in Fig. 13.

Polyethylene oxide was also used in some preliminary work. However, it was found that polyethylene oxide crystallizes too rapidly so that spherulitic structures are mixed with more-or-less oriented structures, as seen with the polarizing microscope. Polyethylene oxide, being water soluble also presented handling problems. Based on these difficulties, further work in the polyethylene oxides was stopped.

#### 1.6 Preparation and testing of Mylar "T" Film Laminates

Mylar "T" film, obtained from DuPont, is a heat and stress annealed film which is oriented more in one direction than in the other. It was thought that these films might serve as a basis of comparison for the work with the stirrer-induced crystallization films since "T" films are commercially available. Preliminary work involved obtaining a wide angle X-ray scattering pattern, which is seen in Fig. 14 and a section viewed between crossed polarizers is seen in Fig. 15. Samples for stress-strain testing were cut parallel and normal to the direction of higher orientation (H.O.). These were then tested to failure in the Instron at a crosshead speed of .1 cm/min. This was done to see if there was a marked difference

in stiffness and strength. The results are plotted in Fig. 16.

Laminates were then prepared from this film. Two-ply laminates were made up with the directions of orientation normal to each ply. Three-ply laminates were constructed in the same fashion as shown in Figs. 17 and 18. Samples were cut from these laminates at angles of  $0^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$ , and  $90^\circ$  relative to orientation axes. The results of the stress-strain curves are seen in Figs. 19-28.

### 1.7 Discussion

The initial attempts at producing an uniaxially oriented film by shear between coaxial cylinders have proved that some orientation can be obtained. This is seen by differences in moduli and tensile strengths on samples tested parallel and normal to the direction of shear (see Fig. 7). By changing the shear rate and temperature, some improvement is seen in tensile strengths and stiffness. Fig. 8 shows the effect of temperature on the stress-strain curves and it is obvious that more perfect crystals are formed when the crystallization temperature is closer to the melting temperature. At lower temperatures, the polymer crystallizes so fast that orientation effects are not dominant. The effect of shear rate on the stress-strain curves in the range shown in Fig. 10 seems to be small.

The effects of washing the film in xylene at elevated temperatures had only a minimal effect on the stress-strain of PE 11774 as seen in Fig. 11. The heat and stress annealing of PE 11173 also showed a marginal effect on the stress-strain curves as seen in Fig. 12. Wide angle X-ray scattering patterns taken before and after annealing showed no improvement in crystallinity or orientation.

It is significant though, that a film was obtained in this preliminary work that according to X-ray scattering patterns (Fig. 9a) has some degree of crystal orientation. However, the films lacked good integrity.

Comparisons of the X-ray scattering patterns between the best polyethylene sample (Fig. 9a) and the commercially obtained "T" film (Fig. 14) were encouraging. The "T" film is marketed as an uniaxially oriented film suitable for magnetic and pressure sensitive tapes, yet its X-ray scattering pattern does not reveal more orientation than the best film produced by the stirrer-crystallization method.

The results of the stress-strain curves for the two-ply Mylar laminates as seen in Fig. 23 and the three-ply Mylar laminates as shown in Fig. 28 are about as expected. It can be seen in both cases that in the linear portions of the curves

(at small strains) the moduli are highest when the samples were cut parallel to an H.O. axis (i.e.,  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$ ). It is surprising however, that the samples cut at  $45^{\circ}$  to the H.O. axis show the highest modulus relative to the  $30^{\circ}$  and  $60^{\circ}$  cut angles.

### 1.8 Future Work in Producing Oriented Films

It is obvious then that the additional driving force of pressure is needed for more orientation and perhaps better integrity. The recently received top stirred reaction vessel, should fulfill these requirements (see Fig. 29). It has been fitted with a cylindrical stirrer and can be pressurized up to 5000 psi at  $100^{\circ}\text{C}$ . It is felt that the additional pressure applied to the solutions which have been used in this report should result in more oriented films.

## 2. SCREENING OF POLYMERS FOR EASILY ORIENTED EXTENDED CRYSTALS

### 2.1 Introduction

While it was known that polyethylene and polyethylene oxide did form extended chain crystals under shear or high pressure, it was not known if other more rigid polymers might be crystallized in an extended form under less drastic conditions. Therefore it was proposed in the contract that more rigid-like polymers be examined to see if extended and oriented chain

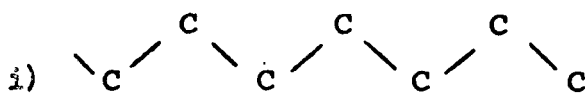


crystals could be formed.

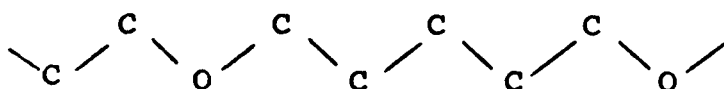
Two decisions were made to hasten this screening of materials. It was decided that ultra-thin film casting might be an effective screening method for determining quickly whether oriented structures could be formed. Secondly three classes of material were selected for preliminary screening: i) a flexible polymer-polystyrene; ii) a semi-stiff polymer-cellulose acetate; iii) a rigid polymer-poly-alkyl-isocyanate.

The first class of polymers is like those of polyethylene and polyethylene oxide in having a rather flexible chain backbone. However the polystyrene was atactic and couldn't crystallize so that the attempt was to examine the effect of ultra-thin casting on non-crystalline ordering. The cellulose acetate does crystallize and can give rather strong crystalline peaks although there is still some amorphous material. The poly-alkyl-isocyanates are known to be rigid rods<sup>20</sup>. These materials are highly crystalline and would be expected to form an ordered liquid structure under even a small shear gradient. These materials are like polypeptides

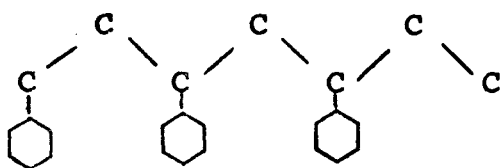
materials that are known to be helix forming even in solution.



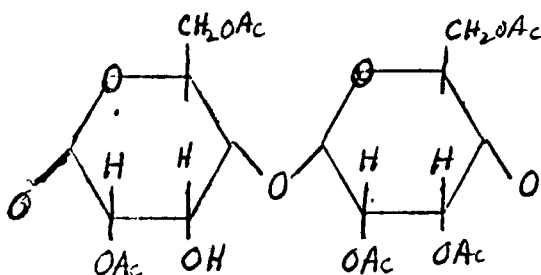
polyethylene



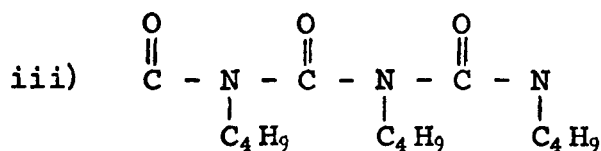
polyethylene oxide



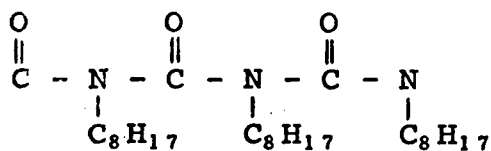
polystyrene



cellulose acetate



polybutylisocyanate  
(PBIC)



polyoctylisocyanate  
(POIC)

It was hoped that even more extended rigid polymers like the polybenzimidazoles or Kevlar could be handled in this form for screening. Unfortunately none of the materials showed any significant promise when prepared by the ultra-thin film casting techniques. It appears that all of the materials will have to be prepared by the pressure-stirring technique if they are to be truly oriented as extended-chain crystals.

However, there was a need to know more about the structures of PBIC, since this material almost certainly could be oriented as an extended chain. For this purpose X-ray diffraction studies were made of samples prepared in the bulk state. The melting point is very close to the temperature at which chain degradation begins so that care must be taken not to destroy the small research samples that were given to the grant through the generosity of Professor L.J. Fetters of the Institute of Polymer Science. The molten sample under no external stress showed no orientation. However, the sample pulled from the melt on a pin and subject only to the internal stress of its own viscous forces did show orientation.

If larger amounts of material can be obtained, the PBIC has great promise when the stirred, high pressure reactor is used for the crystallization. Further X-ray work is being carried out so that the degree of orientation and change in structure can be quickly determined on samples from the reactor.

## 2.2 Poly(n-alkyl isocyanates)

Ultra-thin films of poly n-butyl isocyanate (PBIC) were cast from dilute benzene solutions using a glass-plate dipping technique. The equipment used was 2 x 10 inch glass plates, a tall container for the polymer solution and a drive mechanism to introduce and withdraw the glass plates from the solution. The whole assembly is shown in Fig. 31. The thickness of the films obtained is on the order of 250 Å. Three hundred layers of these ultra-thin films were stacked together and examined by stress-strain measurements. A comparison of the results to that of the films of 0.05 mm. thickness cast by conventional techniques is shown in Fig. 32. It indicates that the thin films have very few different mechanical properties. That is, the ultimate breaking strengths of the ultra-thin films are initially larger than those of the thick films.

However, on repeated stretching the thick films finally achieve the same breaking strength as the ultra-thin films. The initial moduli have not been determined with sufficient precision to determine if there is a significant difference between the two types of films.

X-ray flat plate pictures for ultra-thin and thick films of PBIC are shown in Figs. 33 and 34. Since the poly (n-alkyl isocyanate) molecules exist as rigid rods in solution, it was thought that by thin film casting these molecules should crystallize as extended chains and orient in the spreading direction. Unfortunately, from the X-ray pictures it is seen that no preferred orientation exists in either ultra-thin films or thick films. The corresponding Bragg's spacings are listed in Table III.

Oriented specimens of poly(n-alkyl isocyanates) were obtained by simple viscous drawing from the polymer melts. A typical X-ray fiber pattern for PBIC is shown in Fig. 35. The equatorial arcings are an indication that the polymer chains have preferentially aligned themselves in the fiber axis. For comparison, Fig. 36 shows an X-ray picture of a randomly

oriented PBIC sample. The corresponding Bragg's spacings for both samples are listed in Table IV. These spacings are in approximate agreement with the data obtained by Shmueli, Traub and Rosenheck (1). The structure they deduced is a hexagonal packing of the polymer molecules with unit cell parameters  $a = 13.3\text{\AA}$  and,  $c = 15.5\text{\AA}$ , respectively. An electron diffraction pattern taken from our sample confirms the hexagonal packing as shown in Fig. 37.

Figure 38 shows an X-ray fiber pattern for poly(n-octyl isocyanate) (POIC). The random orientation pattern is shown in Fig. 39. As can be seen, the replacement of the butyl side chain by octyl group does not change the crystal structure to any extent. The corresponding Bragg's spacings are listed in Table V.

### 2.3 Polystyrene

Figure 40 shows that ultra-thin films cast from an amorphous polymer exhibit little significant mechanical difference when examined either parallel or perpendicular to the casting direction or when compared to thick films.

## 2.4 Cellulose Acetate

Figures 41 and 42 indicate that the ultra-thin films cast from cellulose acetate also do not show any significant difference in mechanical properties when examined parallel or perpendicular to the casting direction, or when compared to thick films.

### References

1. Sakurada, I., T. Ito and K. Nakamae, J. Polymer Sci., C, 15, 75 (1966).
2. C.W. Bunn, Trans. Faraday Soc., 35, 482 (1939).
3. C.W. Bunn, Nature, 161, 929 (1948).
4. Sakurada, I., K. Hutino, and A. Okada, Bull. Inst. Chem. Res. Kyoto Univ., 23, 78 (1950).
5. L.R.G. Treloar, Polymer, 1, 95 (1960).
6. T. Shimanouchi, M. Asahina, and S. Enomoto, J. Polymer Sci., 59, 93 (1962).
7. T. Miyazawa, paper presented at the 13th Symposium on High Polymer Chemistry under the auspices of the Chemical Society of Japan and the Society of Polymer Science, Tokyo, November 1964.
8. H. Tadokoro, T. Yasumoto, S. Murahashi, and I. Nitta, J. Polymer Sci., 44, 266 (1960).
9. M. Asahina and S. Enomoto, J. Polymer Sci., 59, 101 (1962).
10. J.E. Ashton, J.C. Halpin and P.H. Petit, Primer on Composite Materials; Analysis, Technomic Publ. Co., Stanford, Conn. (1969).
11. S.W. Tsai, J.C. Halpin and N.J. Pagano, Composite Materials Workshop, Technomic Publ. Co., Stanford, Conn. (1968).



12. J.C. Halpin and N.J. Pagano, J. Comp. Mat. 3, 720 (1969).
13. J.C. Halpin, K. Jerina and J.M. Whitney, J. Comp. Mat 5, 36 (1971).
14. J.C. Halpin and J.L. Kardos, J. Appl. Phys., April (1972).
15. B. Wunderlich and T. Davidson, J. Polymer Sci. A-2 7 2043-2109 (1969).
16. A. Keller and J. Machin, J. Macromol. Sci, B1, 41-91 (1967).
17. S. Krishnamurthy and D. McIntyre, Reverse Osmosis Membrane Research, ed. H.K. Lonsdale and H.E. Podall, Plenum Press New York, 1972, p. 457.
18. S. Krishnamurthy and D. McIntyre, Polymer Letters, 10 647 (1972).
19. S. Krishnamurthy, D. McIntyre, E.R. Santee, Jr. and C.W. Wilson, J. Polymer Sci., (Phys.) 11, 427 (1973).
20. W. Burchard, Makromol. Chem. 67, 182 (1963).
21. U. Shmueli, W. Traub and K. Rosenheck, J. Polymer Sci., A-2, 7, 515 (1969).

TABLE I  
EXPERIMENTALLY OBSERVED ELASTIC MODULI  
FOR HIGHLY ORIENTED POLYMER CHAIN STRUCTURES

<u>POLYMER</u>	<u><math>E_{11} \times 10^{-6}</math> (psi)</u>	<u><math>E_{22} \times 10^{-6}</math> (psi)</u>
Poly(vinyl alcohol)	36.2	1.54
Polyethylene	34	0.70
Polytetrafluoroethylene	22.2	
Cellulose I	18.5	
Cellulose II	12.7	
Poly(ethylene terephthalate)	10.8	
Polyoxymethylene	7.6	1.12
Polypropylene	6.0	0.42
Poly(ethylene oxide)	1.42	0.56

TYPICAL PROPERTIES OF COMPOSITES

HTS Graphite-Epoxy	21	1.7
Boron-Epoxy	30	2.7
Glass-Epoxy	5.6	1.2

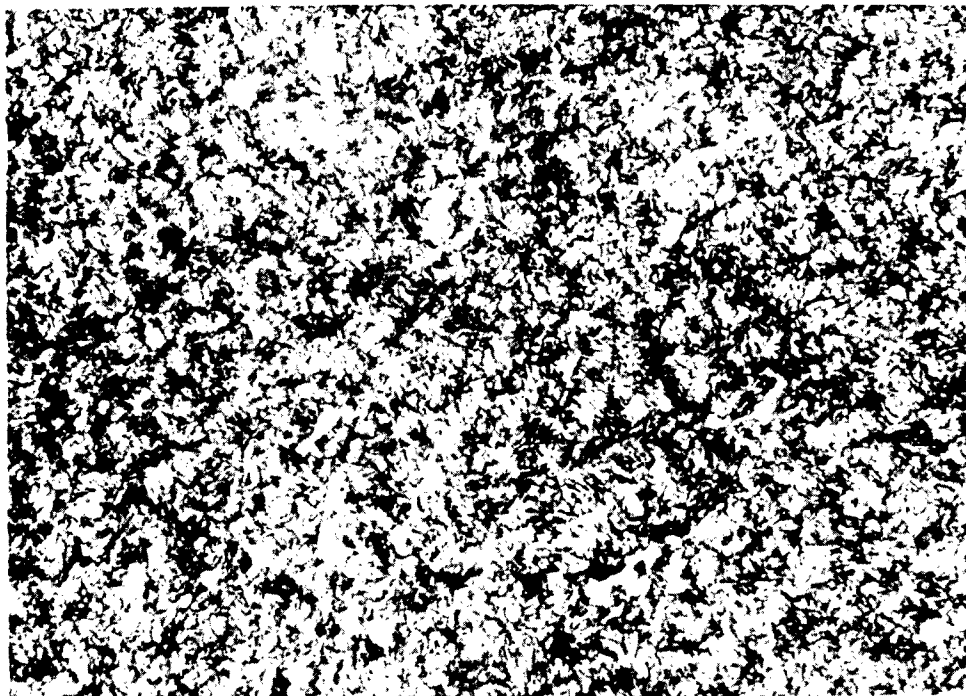
HIGH MODULUS-HIGH STRENGTH ORIENTED ORGANIC FIBER

DU PONT'S' PRD-49

	<u><math>E_{11} \times 10^{-6}</math> (psi)</u>	<u><math>T_b \times 10^{-6}</math> (psi)</u>
Type I	25	3.4
Type III	19	4.0
Type IV	12	4.3

TABLE II  
ELASTIC MODULI  
FOR AN ISOTROPIC LAMINATE  
FABRICATED FROM ORTHOTROPIC SHEETS

	<u>E<sub>11</sub></u>	<u>E<sub>iso</sub></u>	<u>Stress at</u> <u><math>\epsilon=0.007</math></u>
Poly(vinyl alcohol)	36.2x10 <sup>6</sup> psi	14.4x10 <sup>6</sup> psi	~100ksi
Polyethylene	34	13.6	
Boron/Epoxy	30	11.89	83ksi
Polytetrafluoroethylene	22.2		
HTS-Graphite/Epoxy	21	8.96	62ksi
Cellulose I	18.5	~7.6	53ksi
Cellulose II	12.7		
Poly(ethylene terephthalate)	10.8		
Polyoxymethylene	7.6	3.6	
Polypropylene	6.0	2.46	
E-Glass/Epoxy	5.6	2.85	47ksi
Poly(ethylene oxide)	1.42		

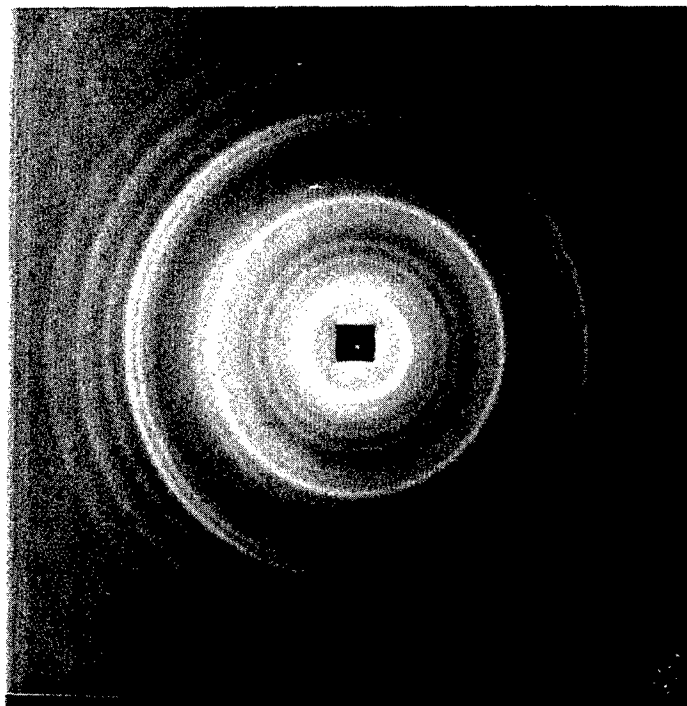


Solution Cast Film of Marlex Polyethylene Randomly  
Crystallized 80 x

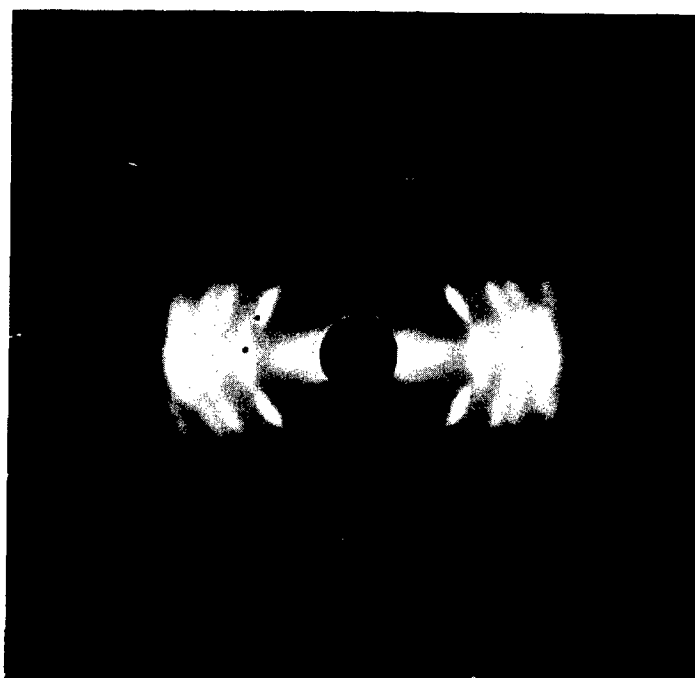


Stirrer-Induced Film of Marlex Polyethylene Crystallized  
In an Oriented Fashion. Shear Direction 160 x

Fig. 2a  
RANDOM AND ORIENTED POLYETHYLENE FILMS OBSERVED  
BETWEEN CROSSED POLARS



Pattern from Random Crystallization



Pattern from Highly Oriented Crystallization

Fig. 2b

WIDE ANGLE X-RAY DIFFRACTION PATTERNS OF RANDOM AND HIGHLY  
ORIENTED CRYSTALLINE POLYMERS

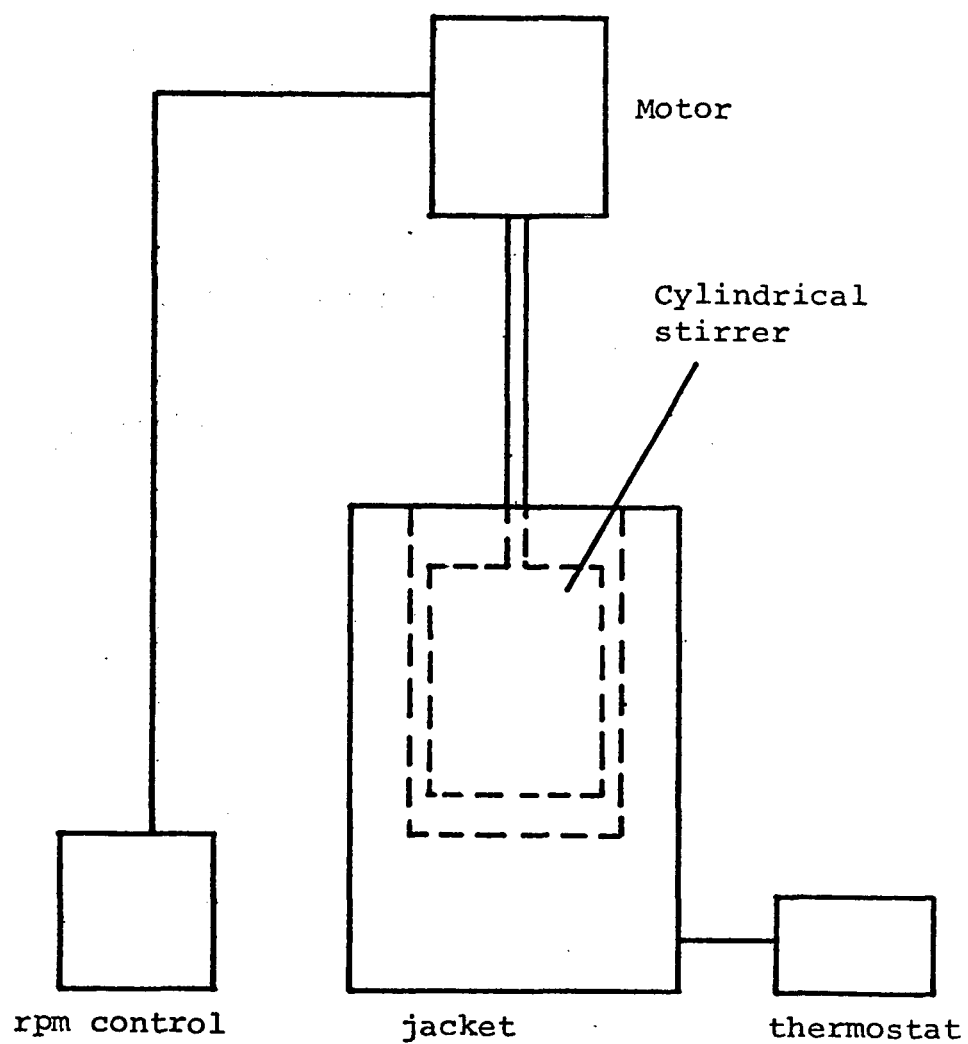


Fig. 3  
STIRRER INDUCED CRYSTALLIZATION APPARATUS

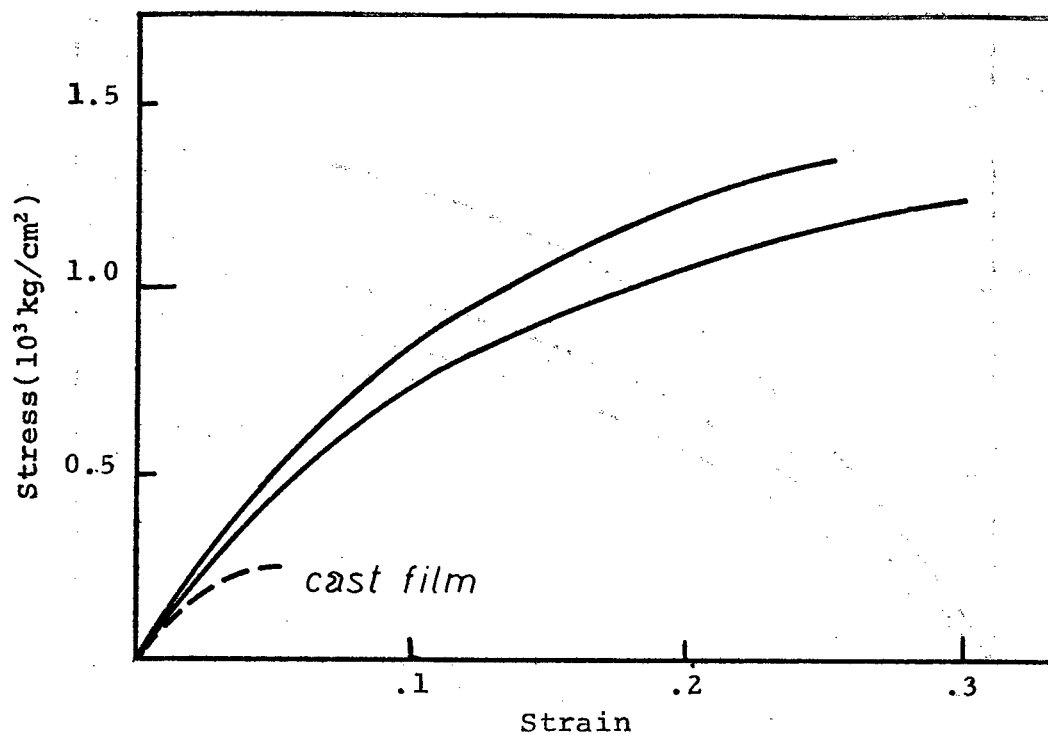


Fig. 4

PE 12574 CRYSTALLIZED AT  $96^\circ\text{C}$

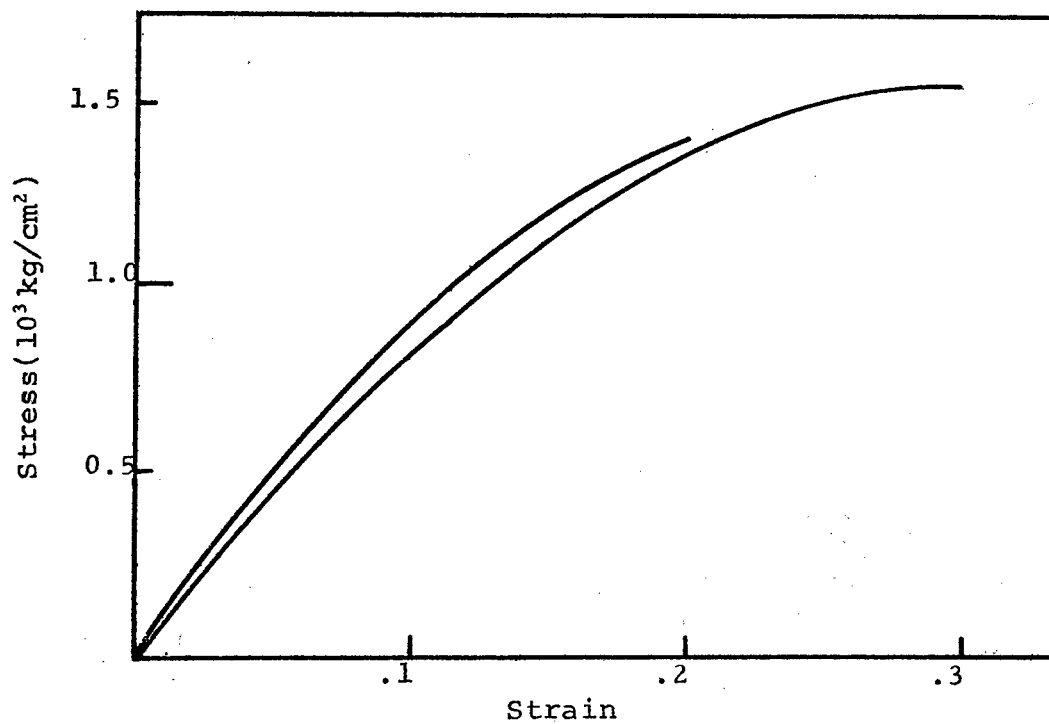


Fig. 5

PE 11774 CRYSTALLIZED AT  $98^\circ\text{C}$

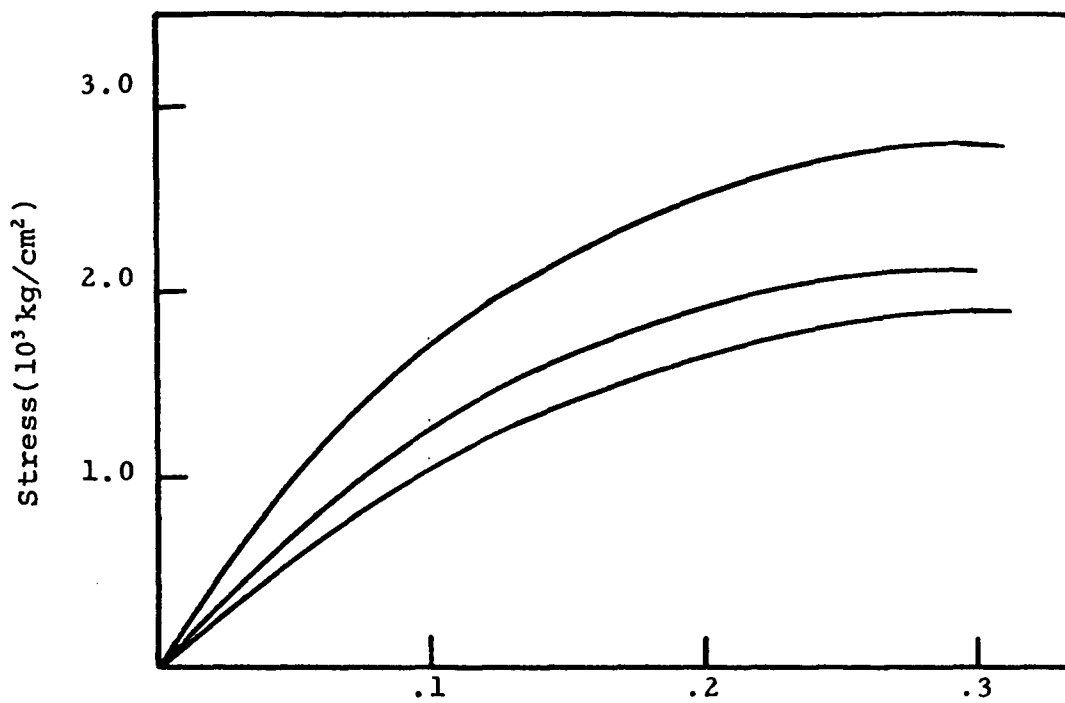


Fig. 6

PE 11474 CRYSTALLIZED AT 100°C

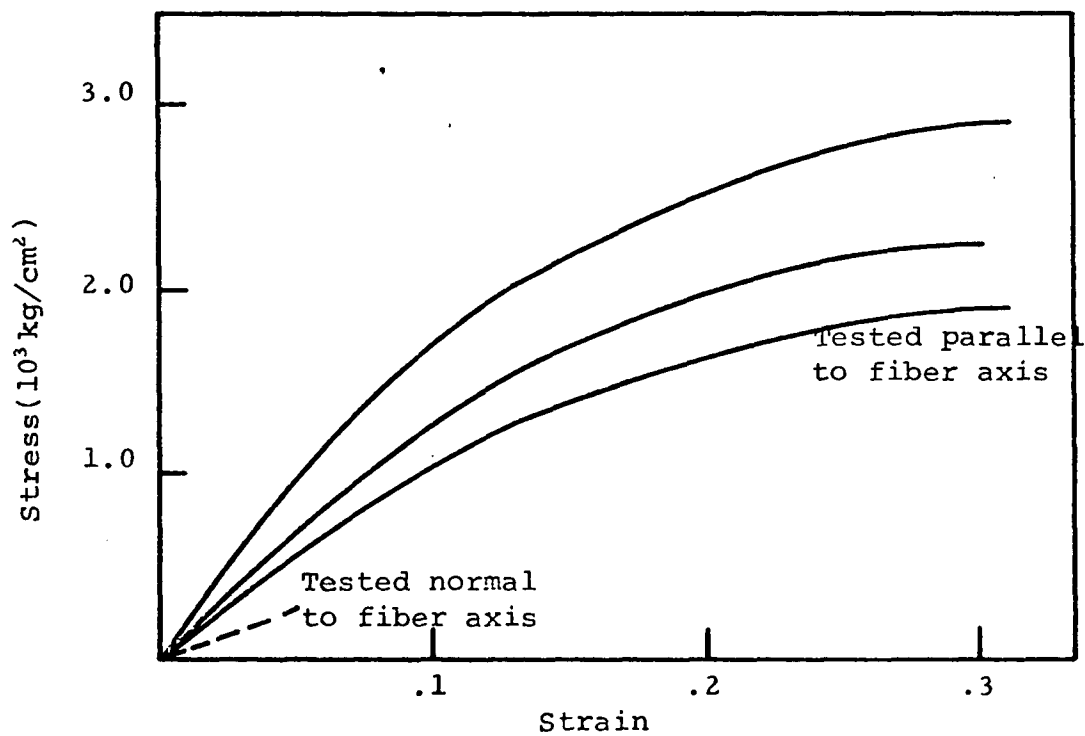


Fig. 7

STRESS STRAIN COMPARISON RELATIVE TO  
ORIENTATION AXIS



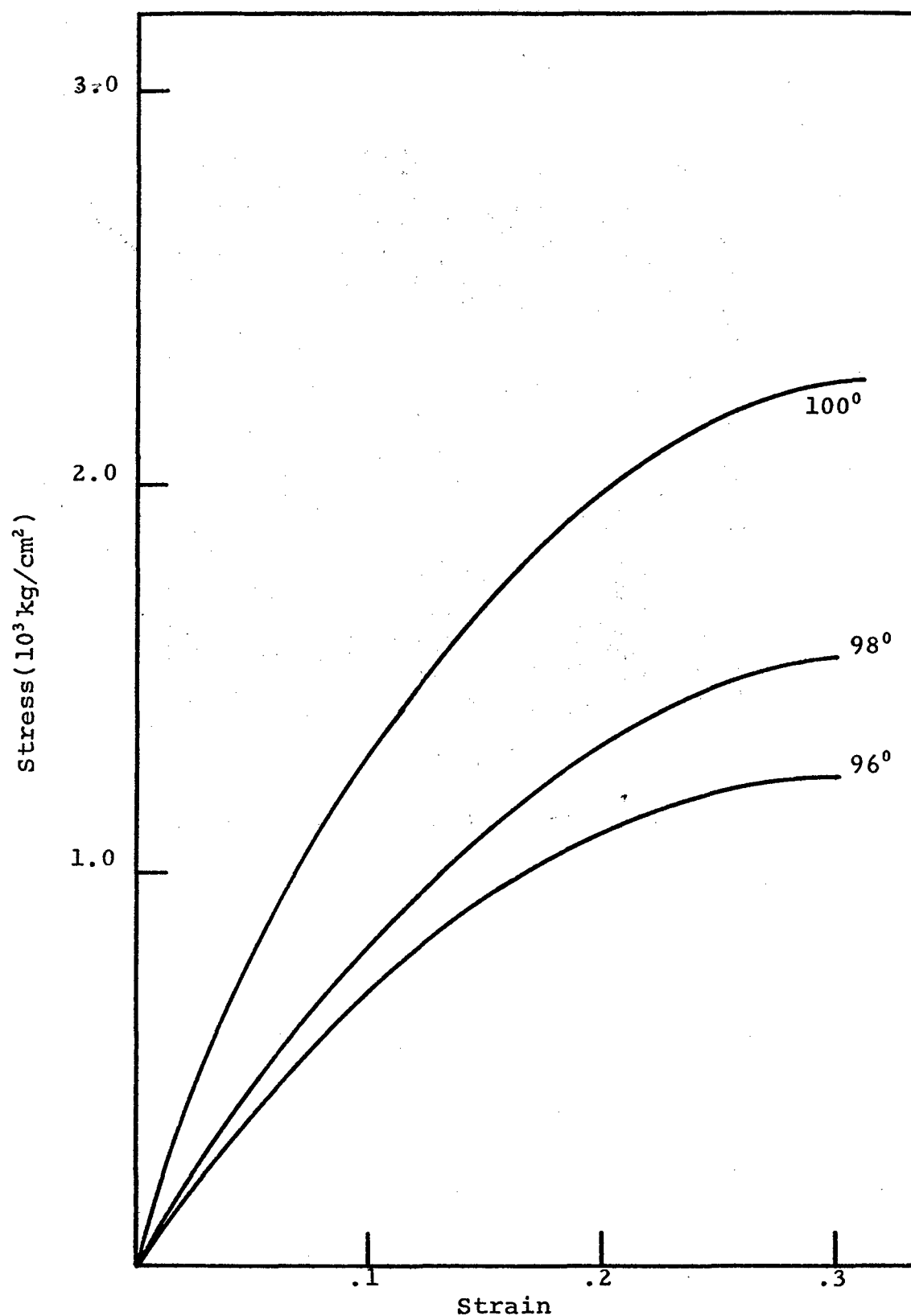


Fig. 8  
STRESS STRAIN AS A FUNCTION OF STIRRER INDUCED  
CRYSTALLIZATION TEMPERATURE

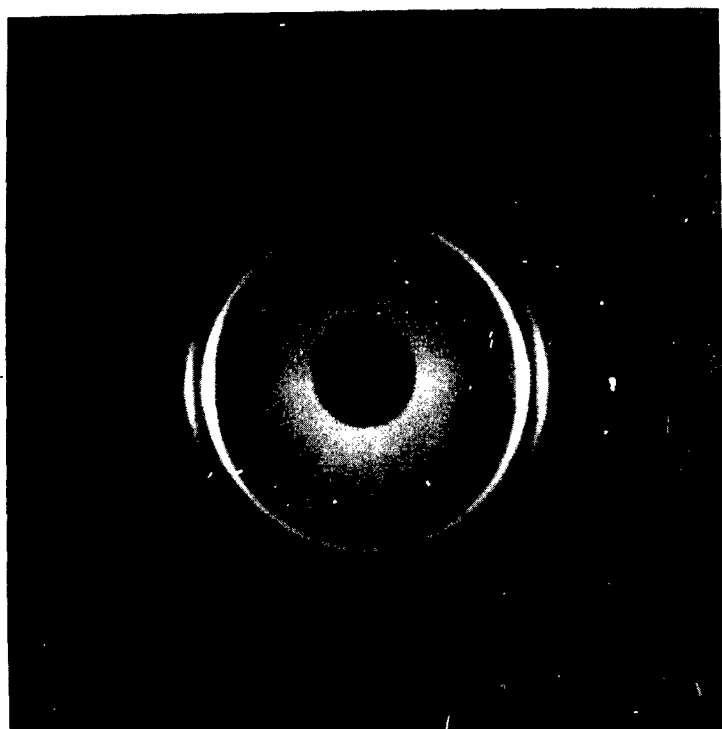


Fig. 9a

WIDE ANGLE X-RAY DIFFRACTION OF PE 11474



Fig. 9b

SCANNING ELECTRON MICROGRAPHS OF PE 11474  
SURFACE FEATURES AT 10,000 x

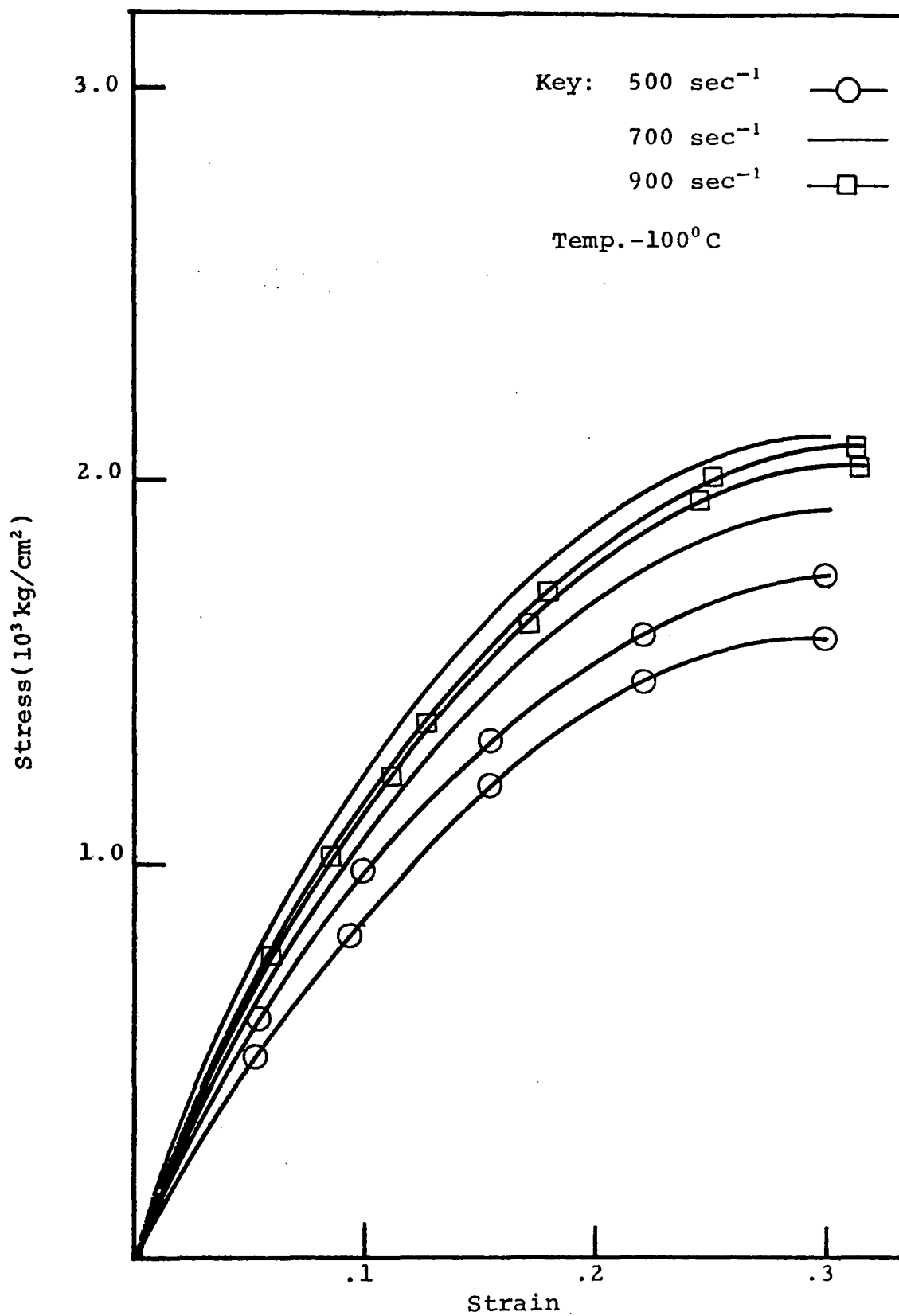


Fig. 10  
EFFECT OF SHEAR RATE ON MECHANICAL PROPERTIES

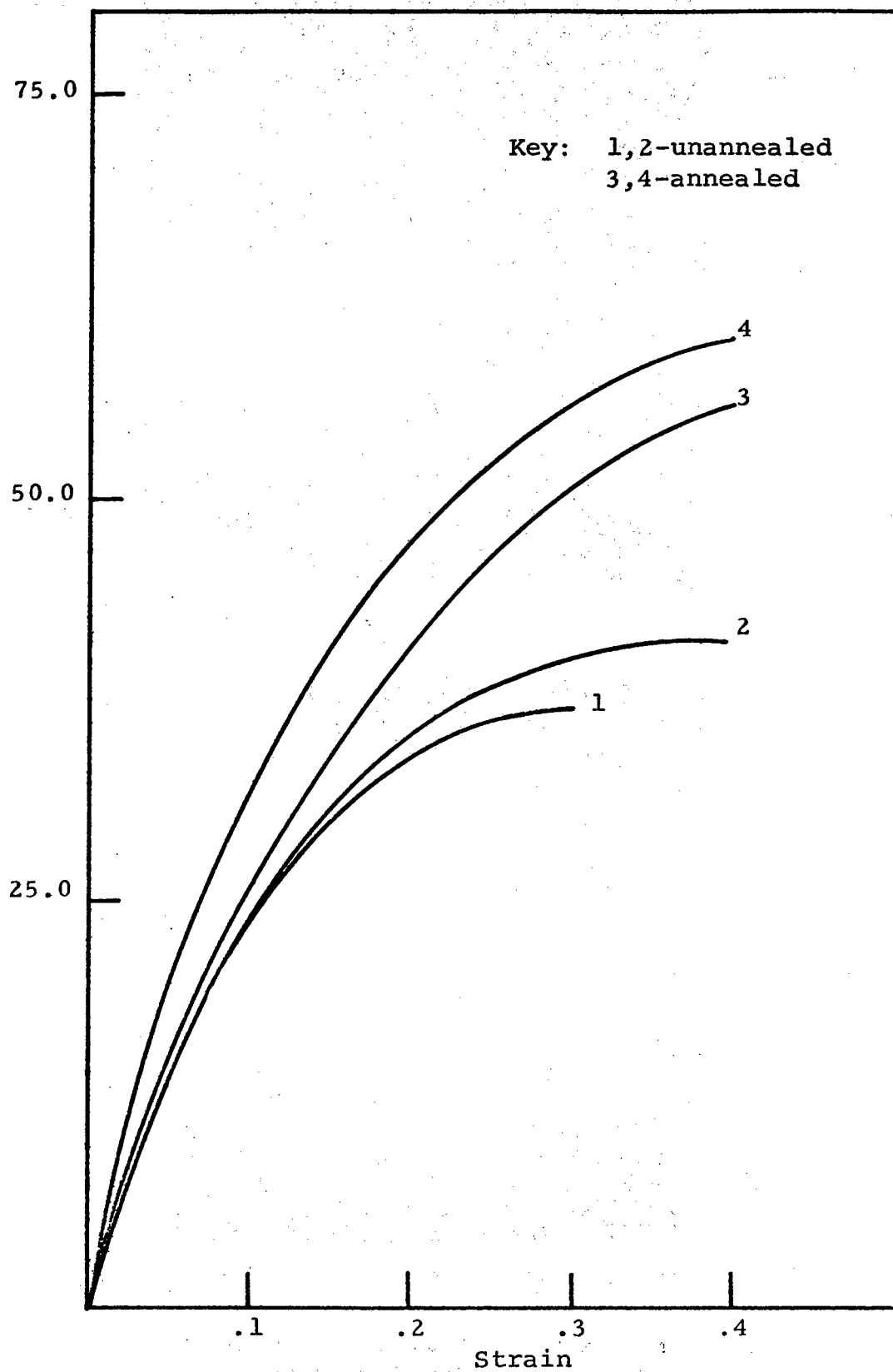


Fig. 11  
EFFECT OF STRESS ANNEALING ON MECHANICAL PROPERTIES

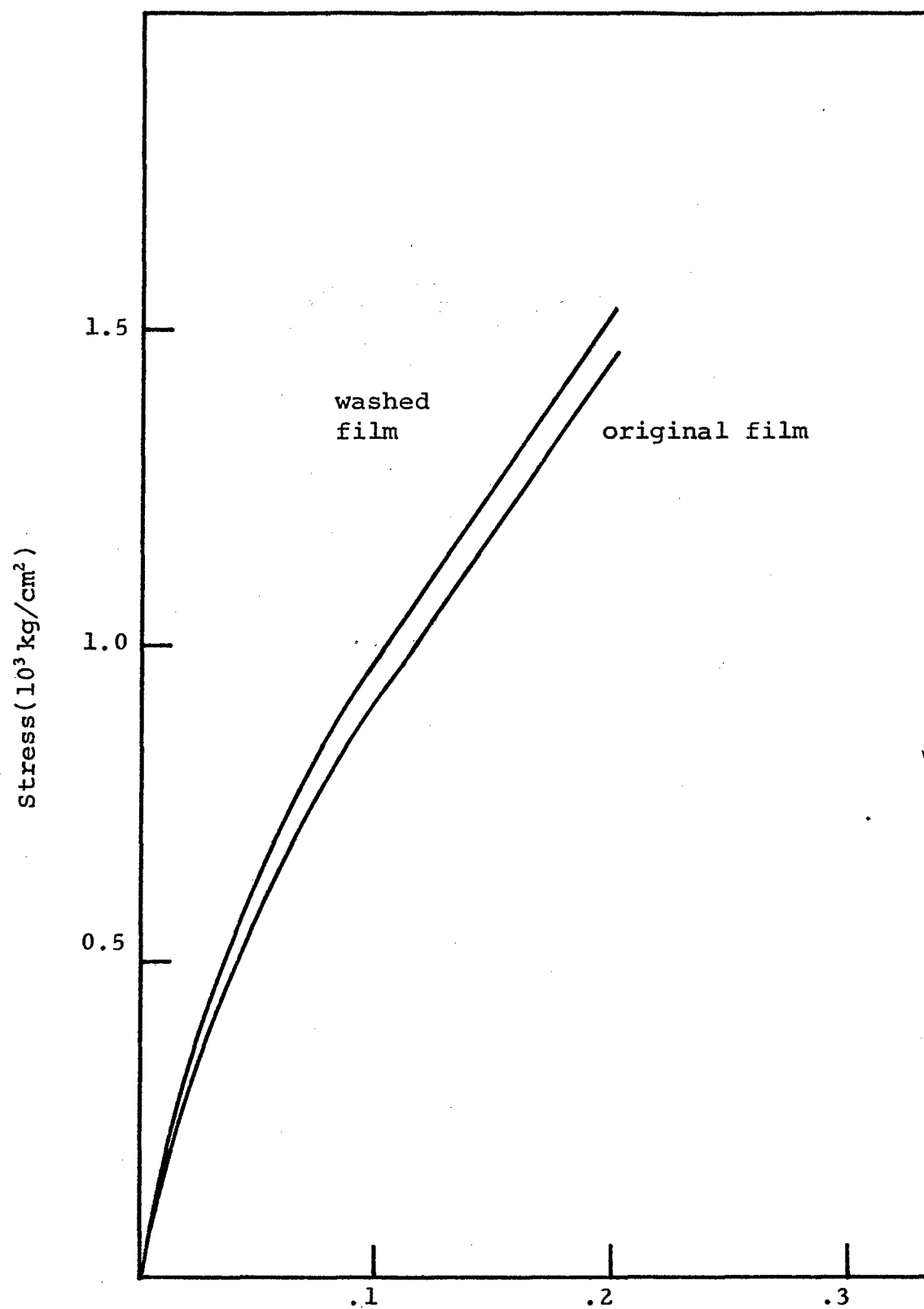


Original Sample



After Annealing for 24 hrs. at 100°C

Fig. 12  
WIDE ANGLE X-RAY DIFFRACTION PATTERNS OF  
UNANNEALED VS. ANNEALED PE 11174



Strain  
Fig. 13

EFFECT OF WASHING UNDER STRESS ON PE 11774

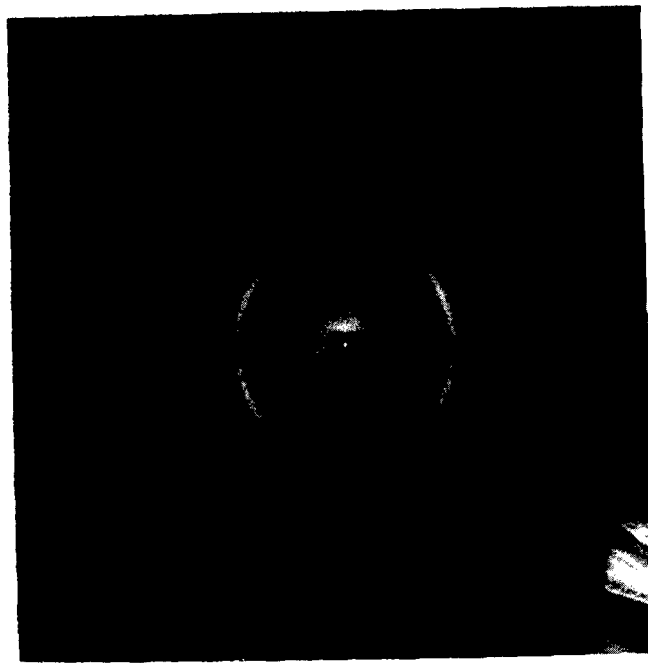
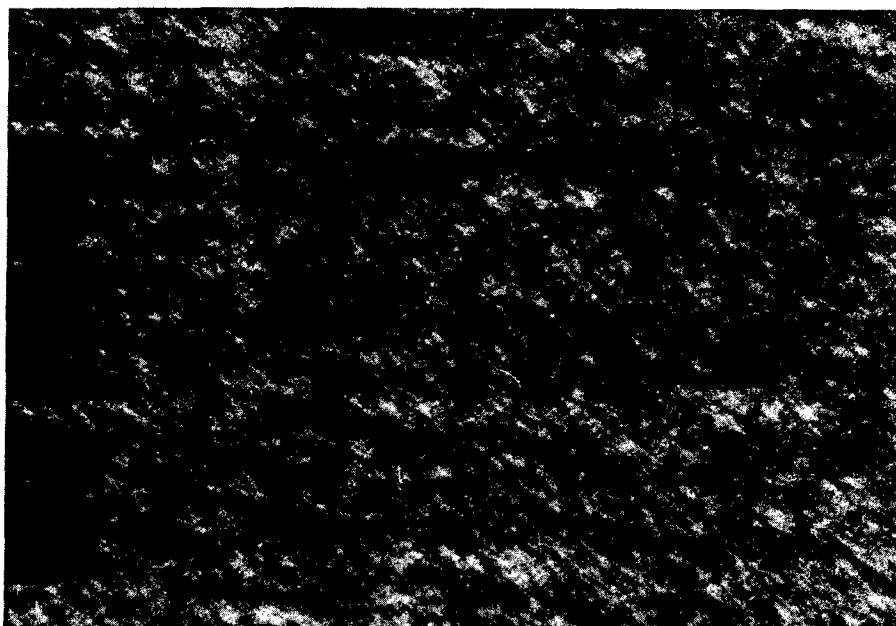


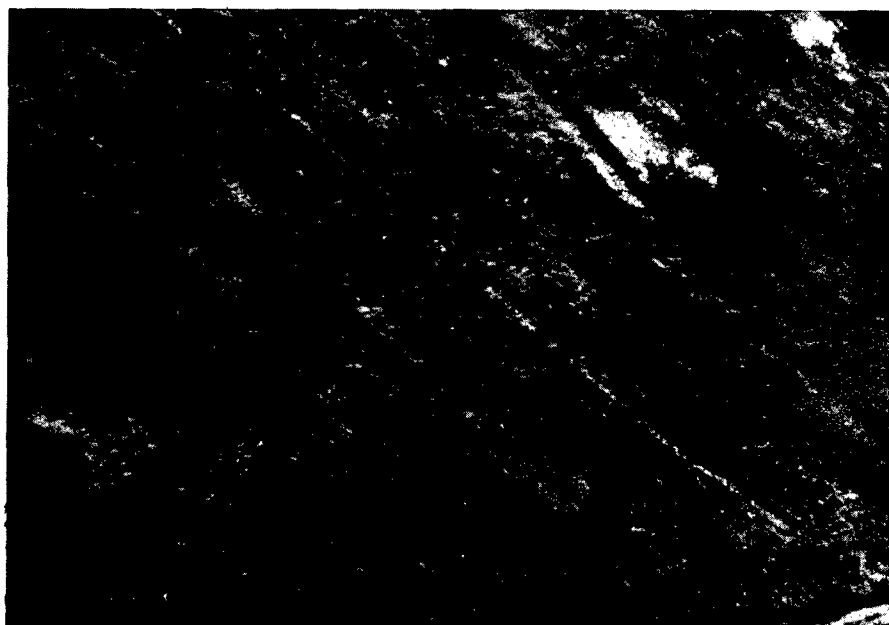
Fig. 14

WIDE ANGLE X-RAY DIFFRACTION PATTERN  
OF MYLAR "T" FILM





80 x



160 x

Fig. 15

MYLAR "T" FILM VIEWED BETWEEN CROSSED POLARS

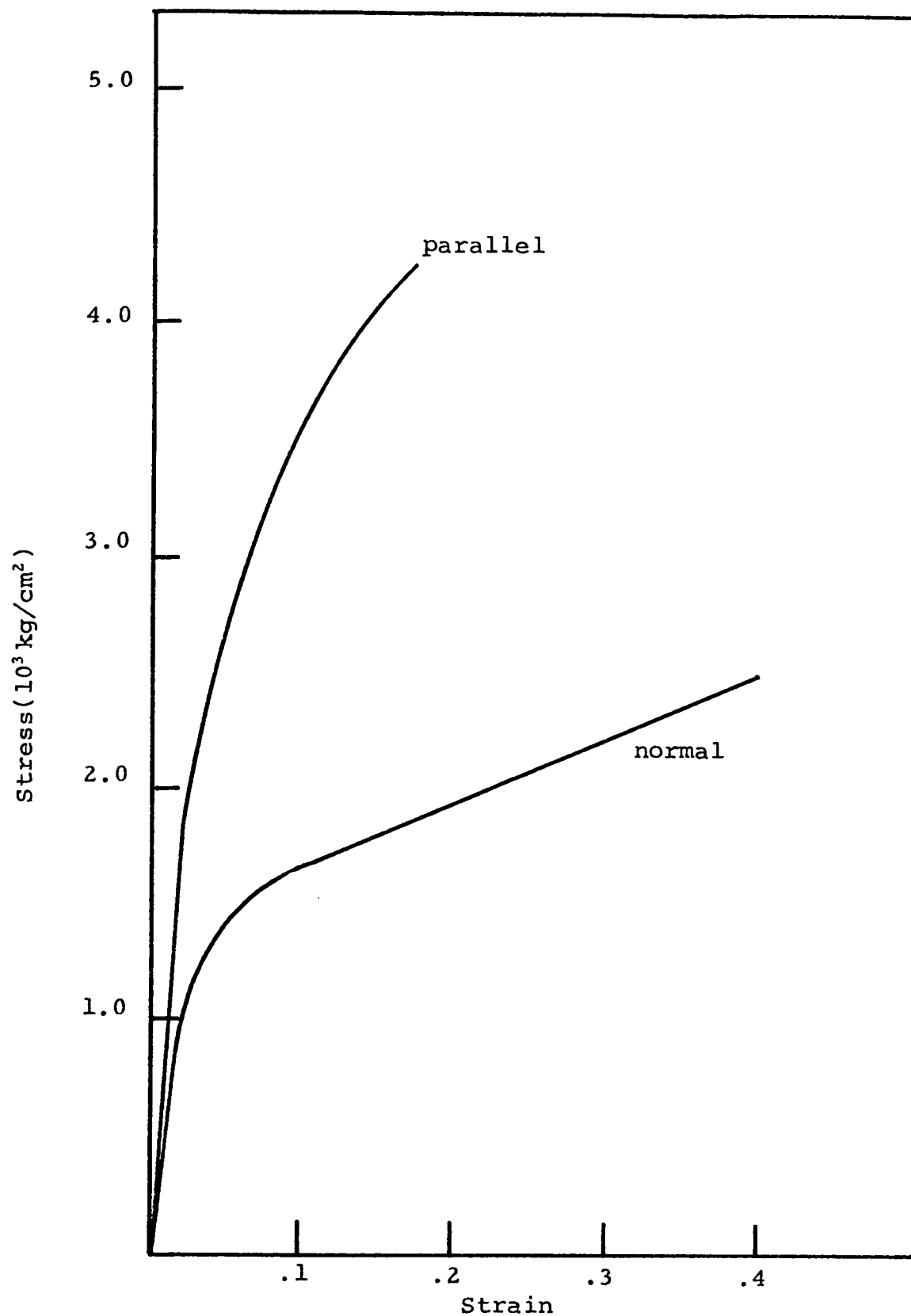


Fig. 16  
STRENGTH OF MYLAR T FILM RELATIVE TO HIGHER  
ORIENTATION AXIS

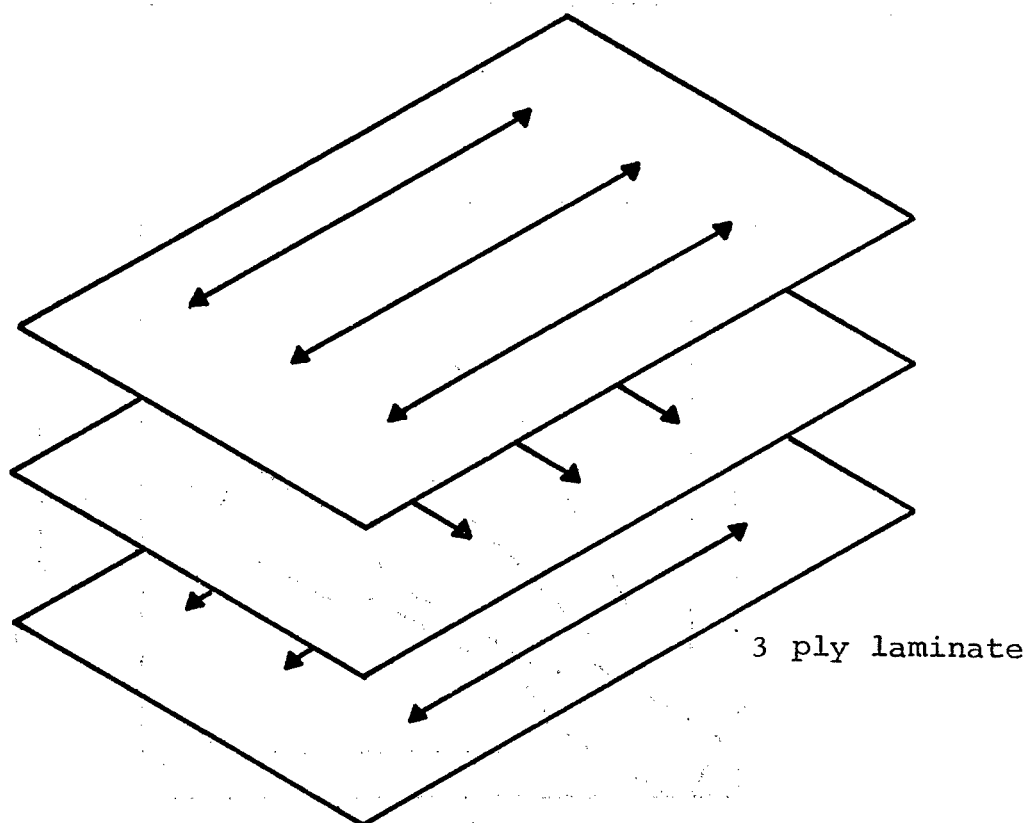
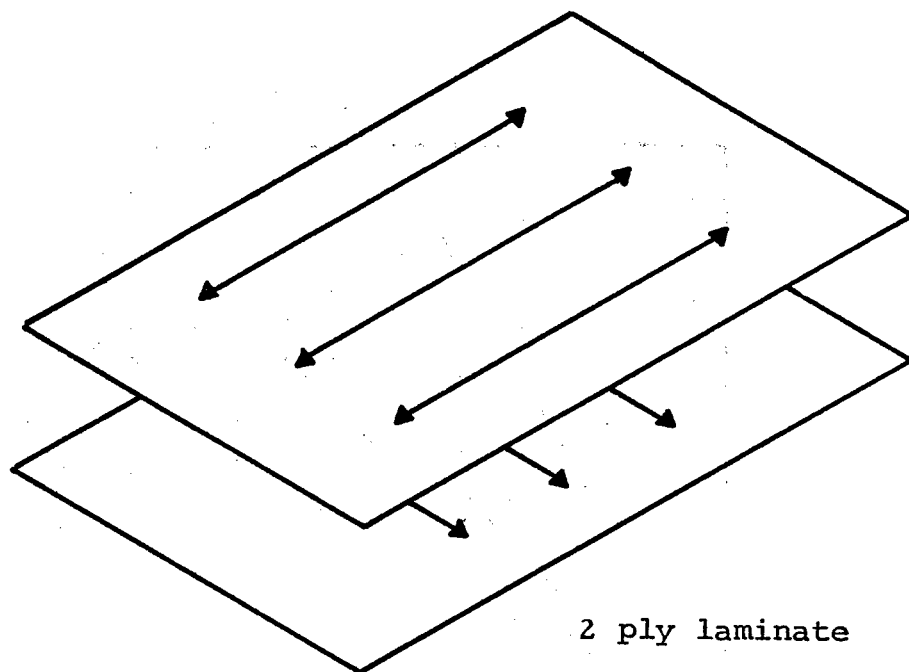


Fig. 17  
SCHEMATIC REPRESENTATION OF "T" FILM LAMINATES  
SHOWING AXIS OF HIGHEST ORIENTATION

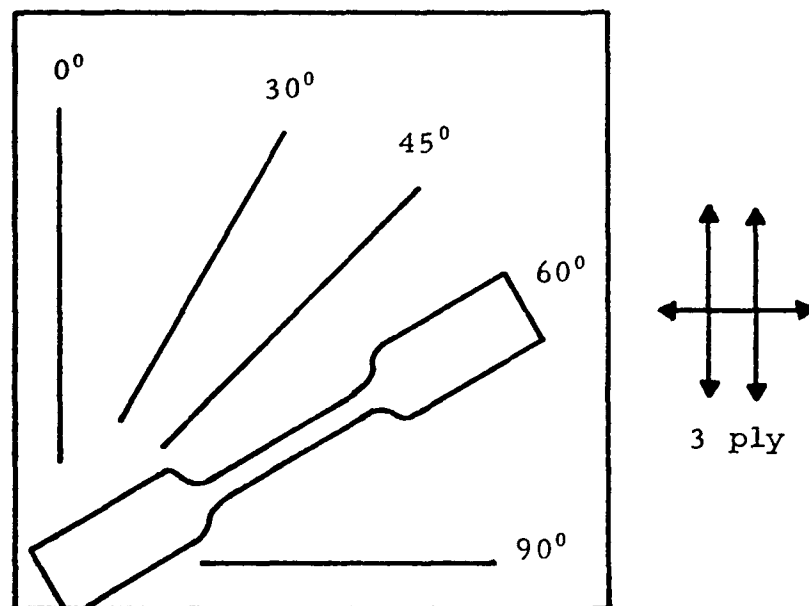
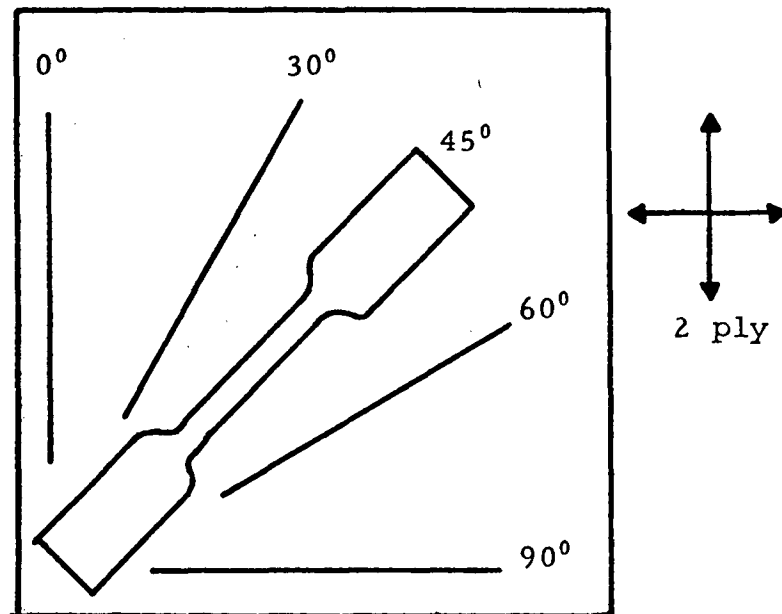


Fig. 18  
 ANGLES OF SAMPLES CUT RELATIVE TO THE HIGHEST  
 ORIENTATION AXES OF THE LAMINATES

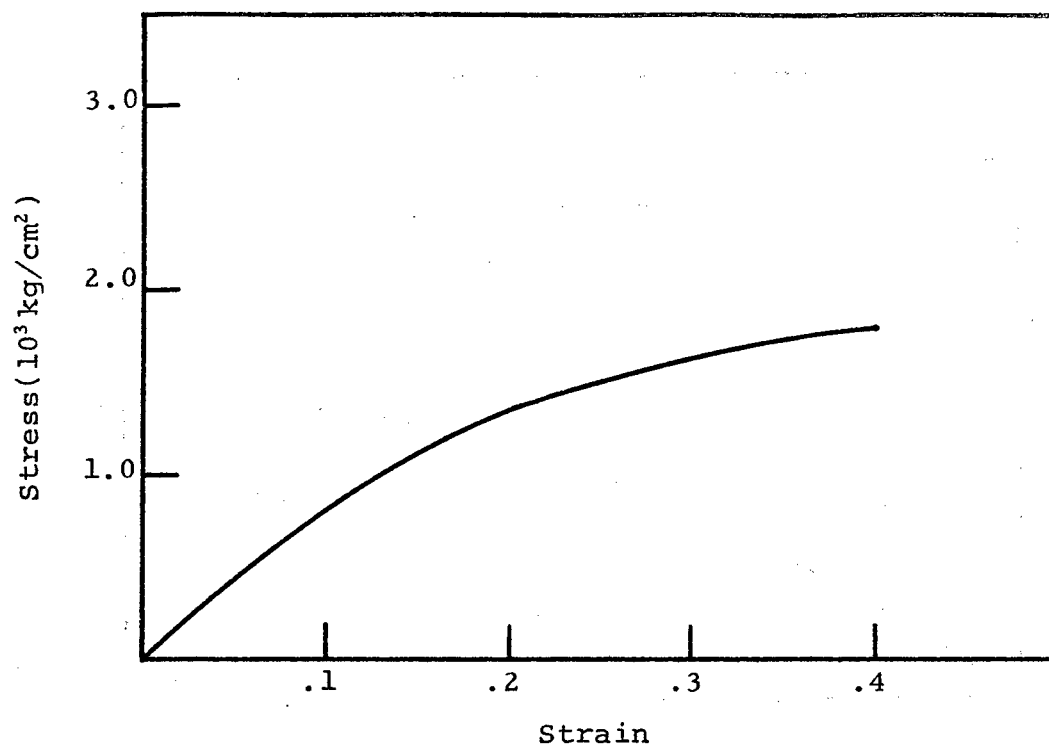


Fig. 19

2 PLY LAMINATE CUT AT 30°

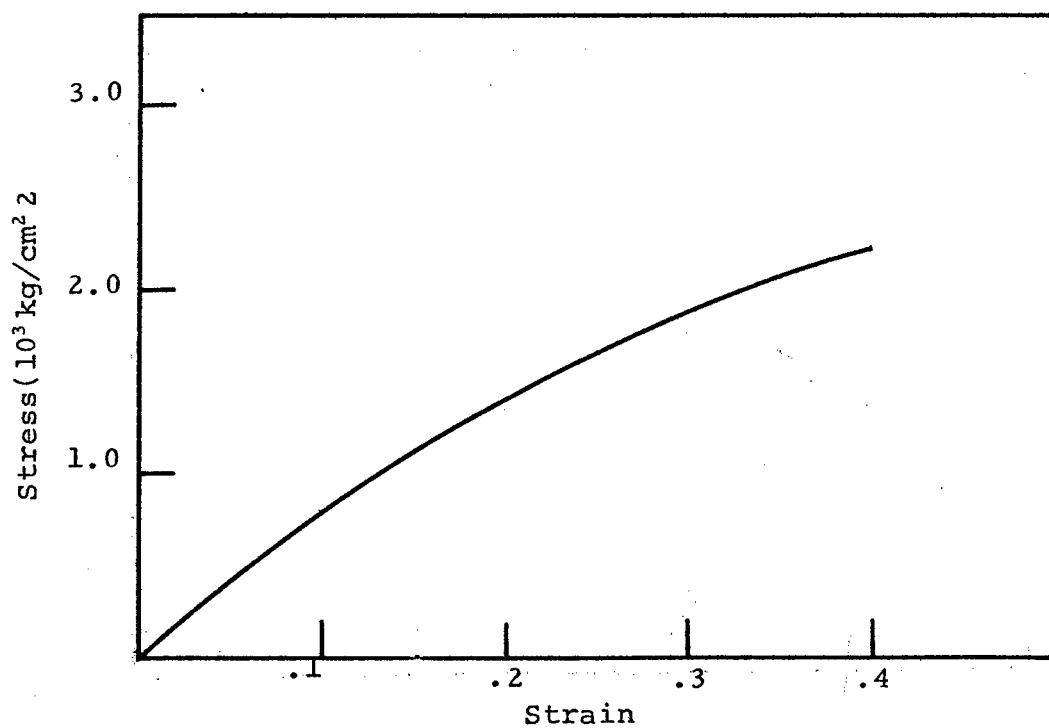
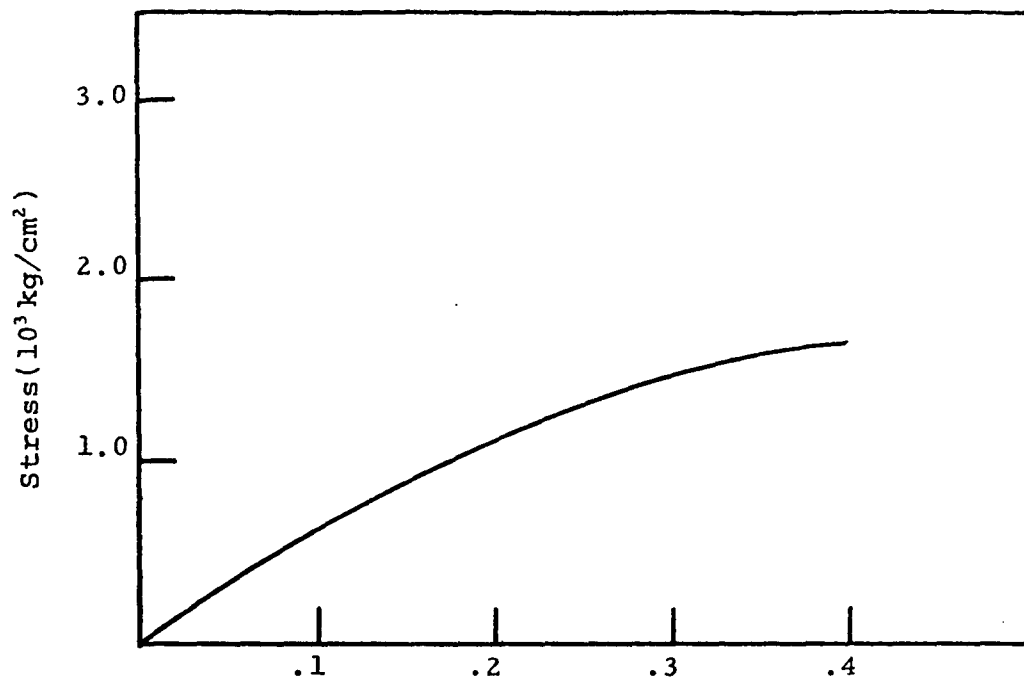


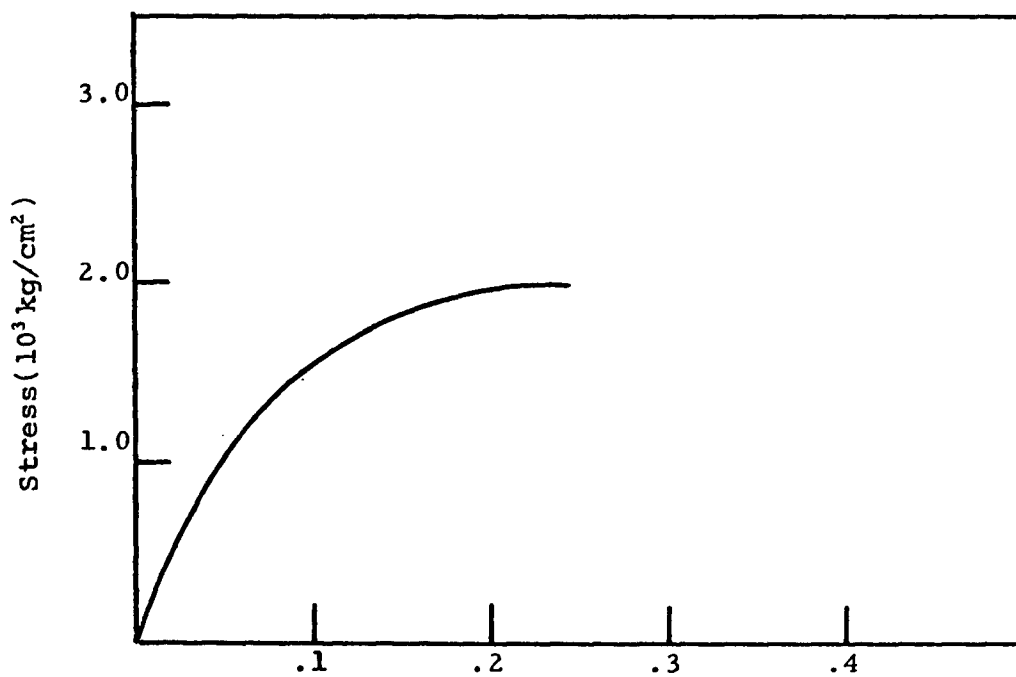
Fig. 20

2 PLY LAMINATE CUT AT 45°



Strain  
Fig. 21

2 PLY LAMINATE CUT AT  $60^\circ$



Strain

Fig. 22

2 PLY LAMINATE CUT AT  $90^\circ/0^\circ$

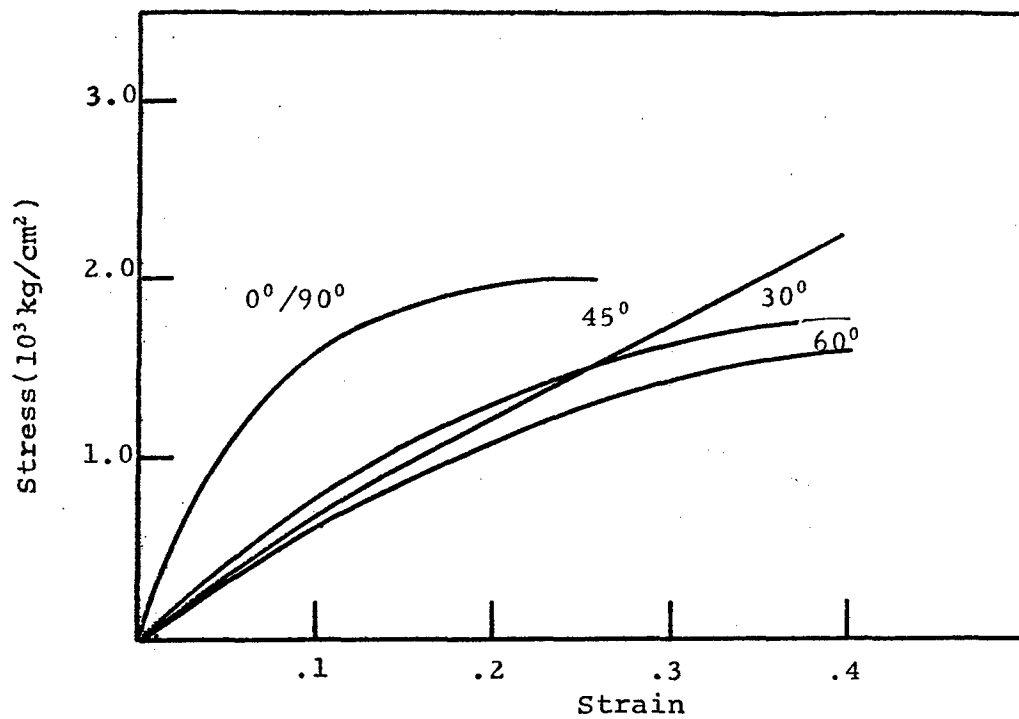


Fig.23

STRESS-STRAIN AS A FUNCTION OF CUT ANGLE FOR  
2 PLY MYLAR LAMINATES

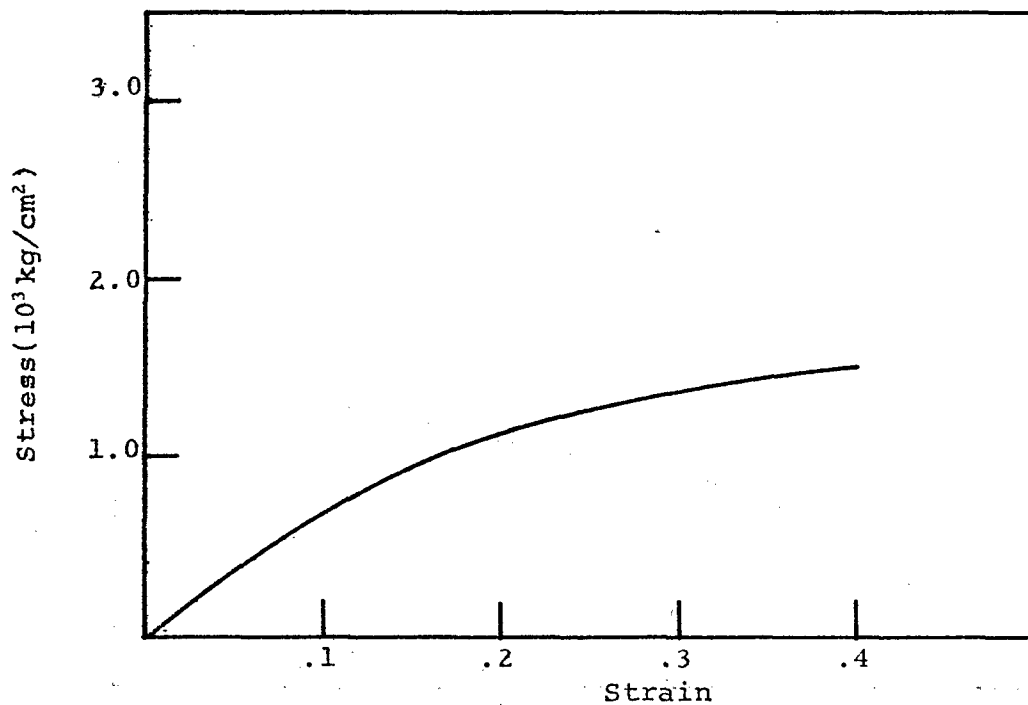


Fig. 24

3 PLY LAMINATE CUT AT 30°

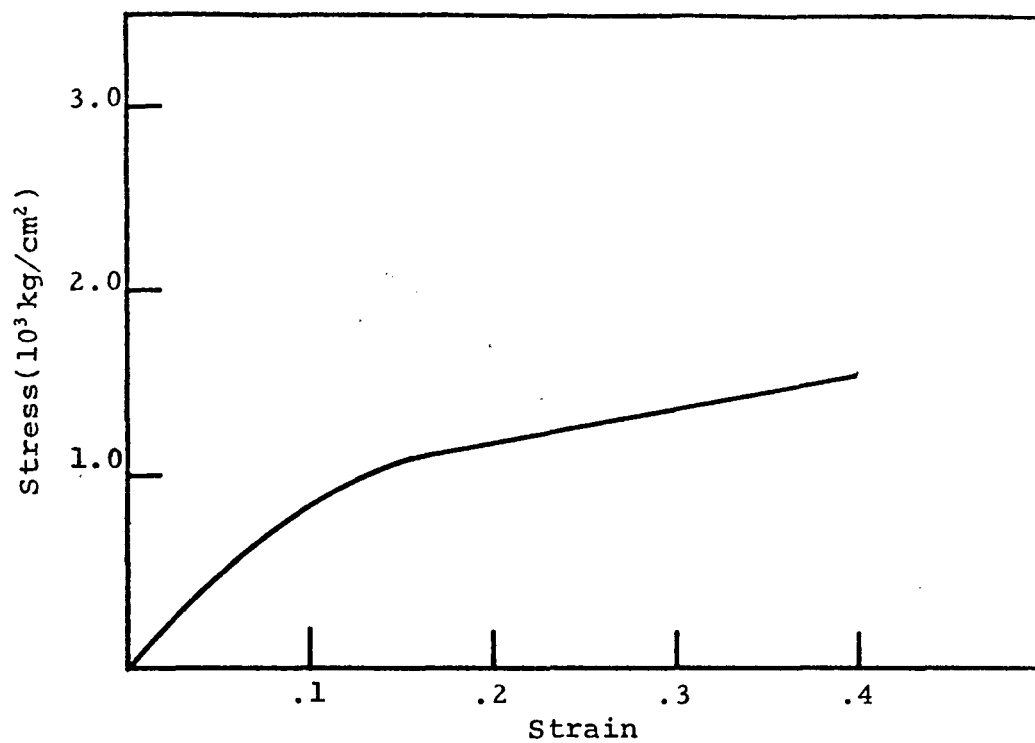


Fig.25

3 PLY LAMINATE CUT AT 45°

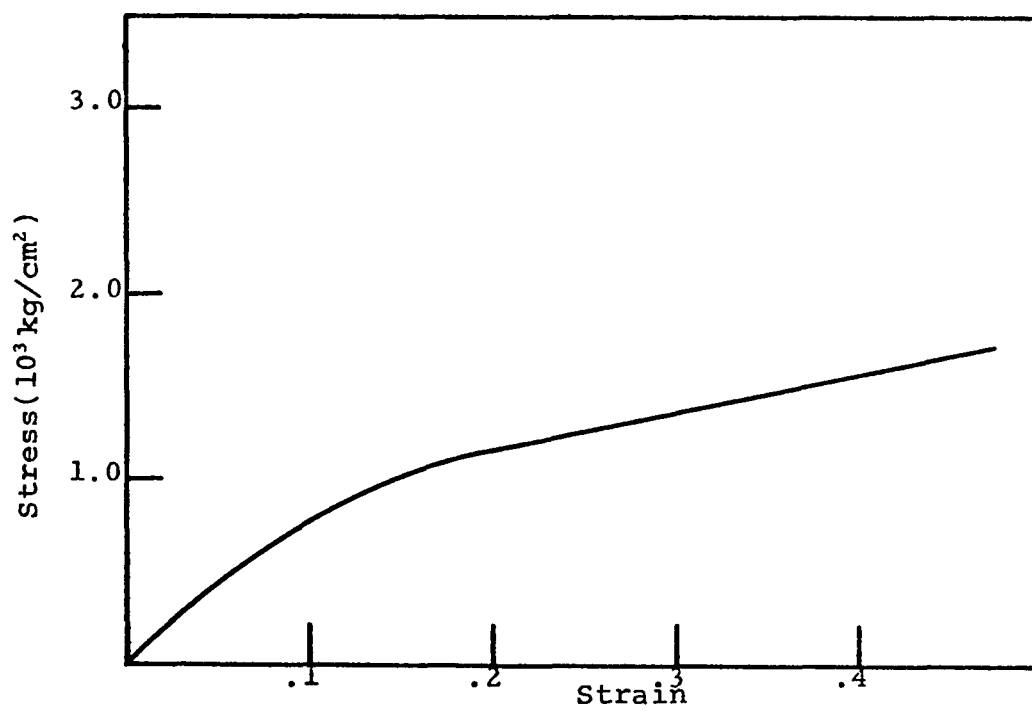


Fig.26

3 PLY LAMINATE CUT AT 60°



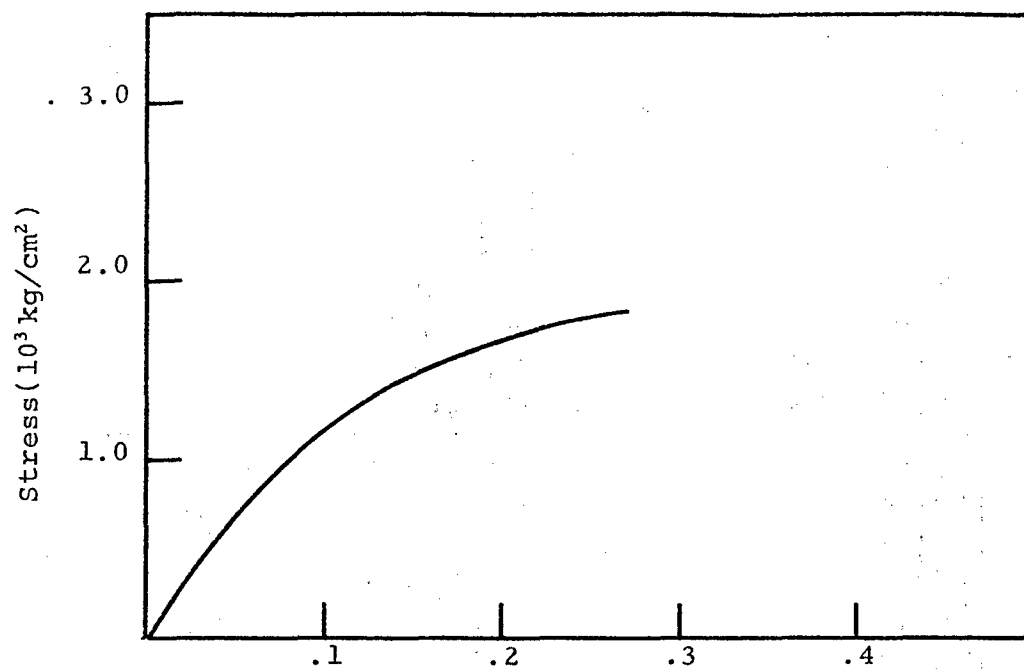


Fig. 27

3 PLY LAMINATE CUT AT 90°

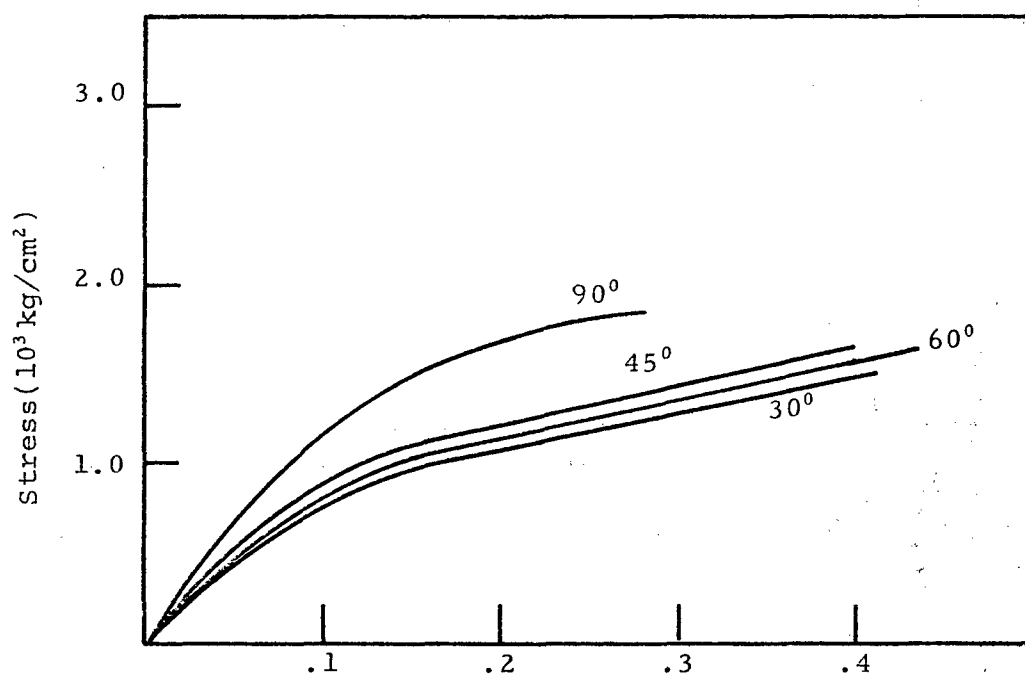
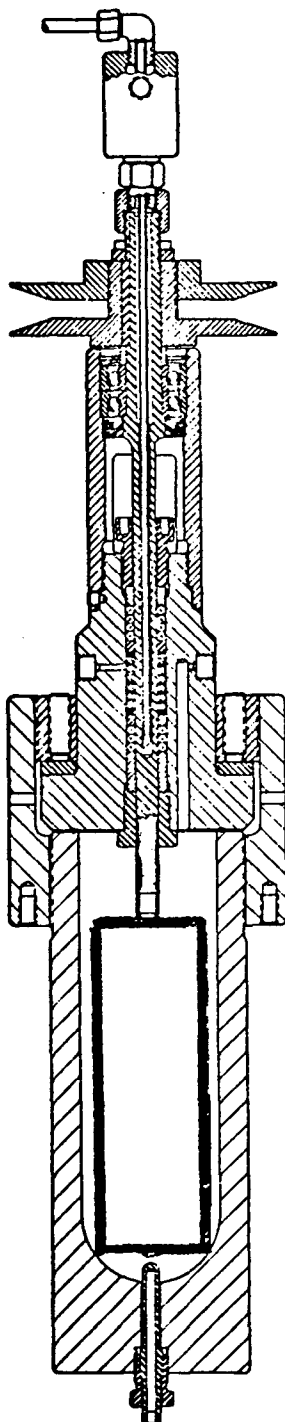
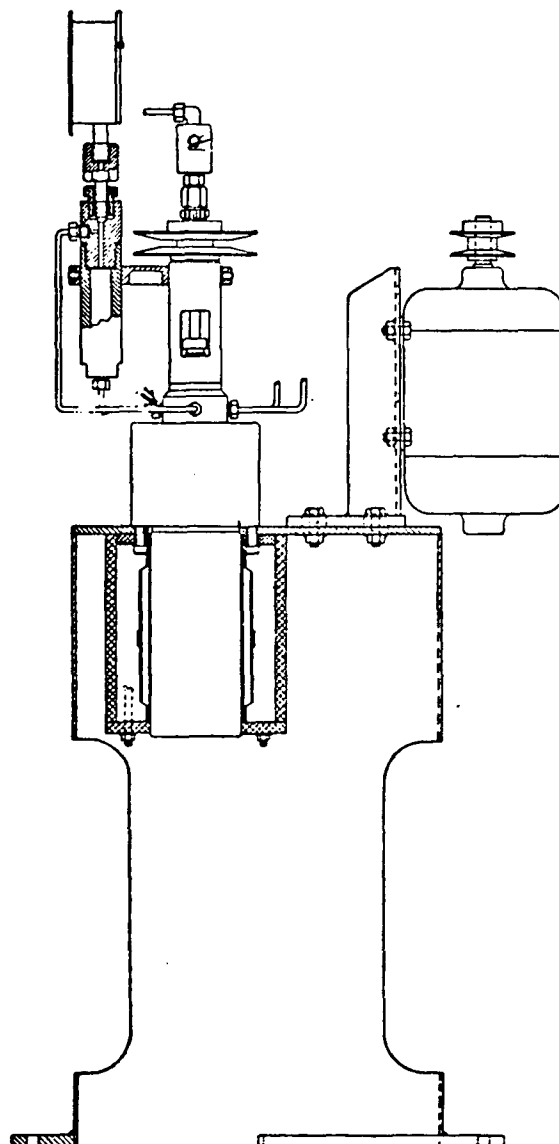


Fig. 28

STRESS STRAIN AS A FUNCTION OF CUT ANGLE FOR  
3 PLY MYLAR LAMINATES



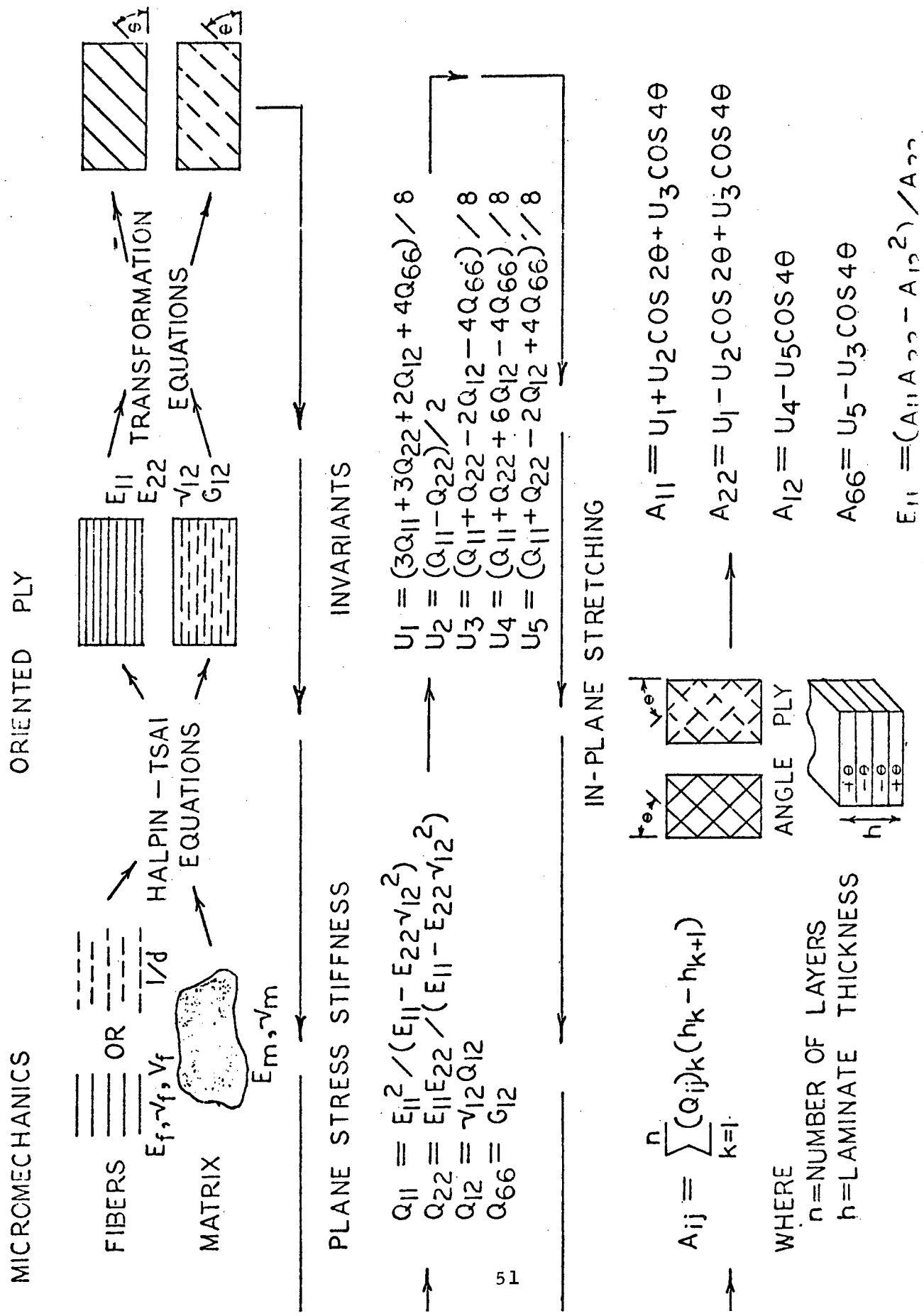
*Schematic of 4 1/2 in. Assembly (Stand furnished but not illustrated.)*



*Schematic of 6 in. Assembly shown mounted in stand.*

Fig. 29  
PRESSURIZED STIRRING REACTOR VESSEL

# LAMINATE CALCULATIONS



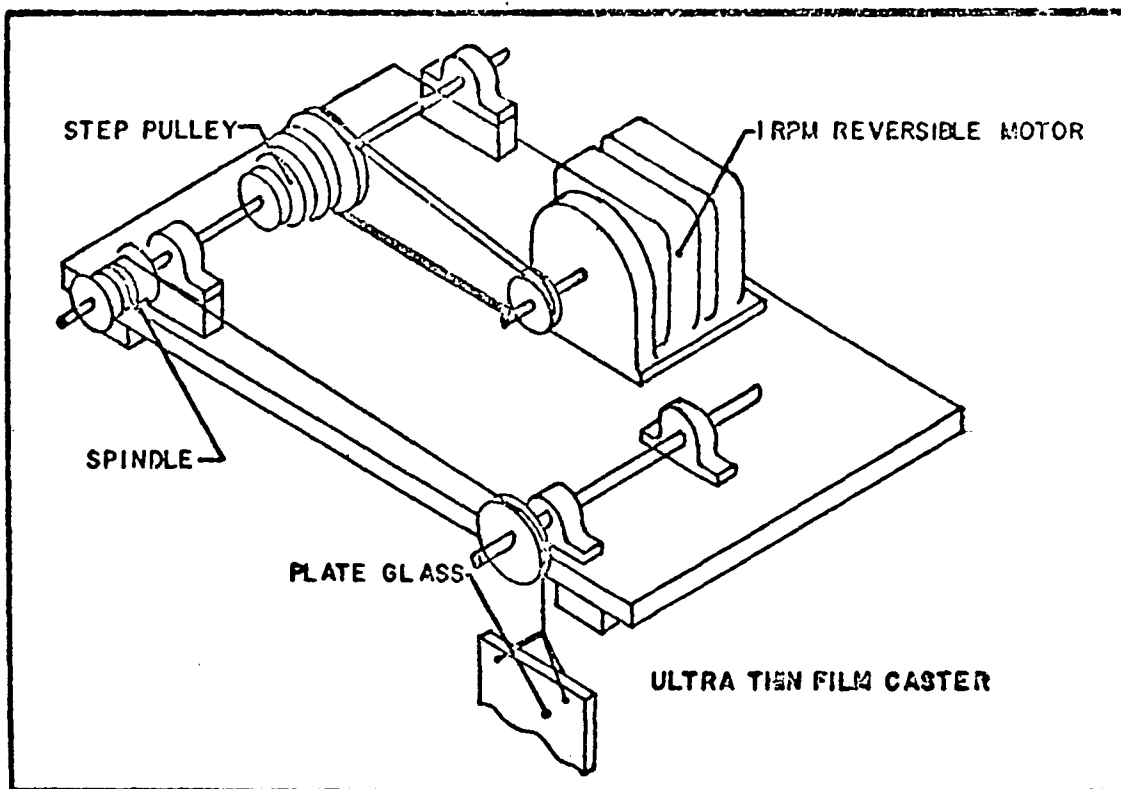


FIGURE 31      ULTRA THIN FILM CASTER

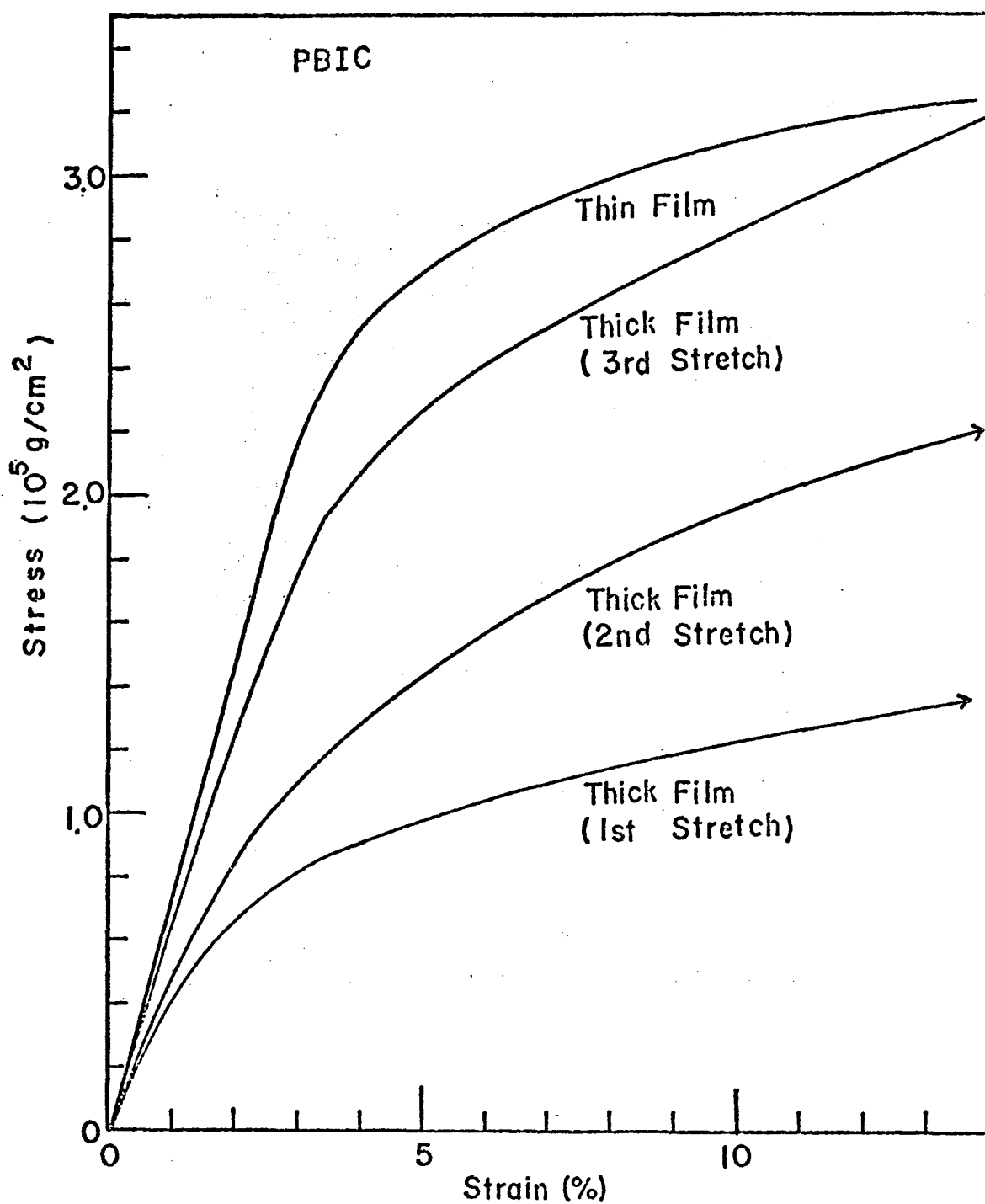


Fig.32. Stress-Strain Curves of PBIC Films

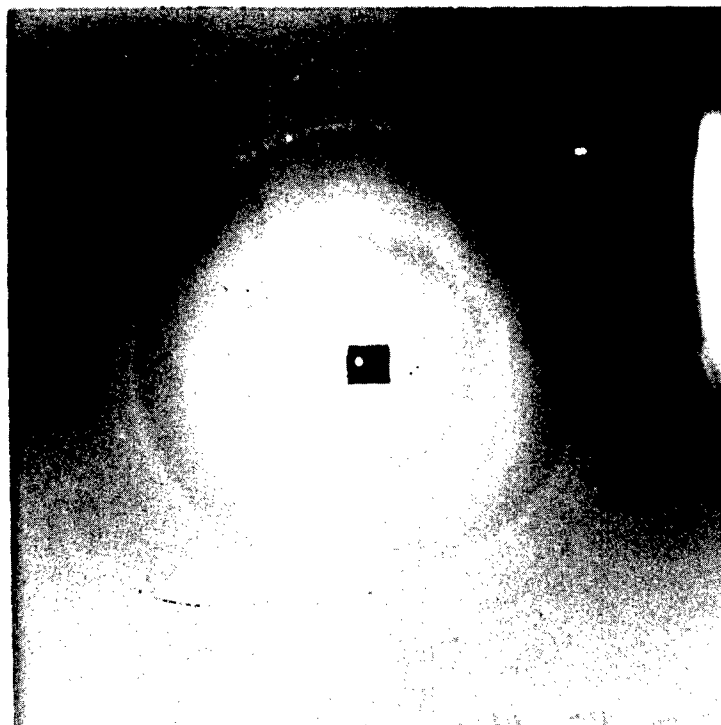


Fig. 33  
X-ray Flat Plate Picture of PBIC Ultra-thin Film

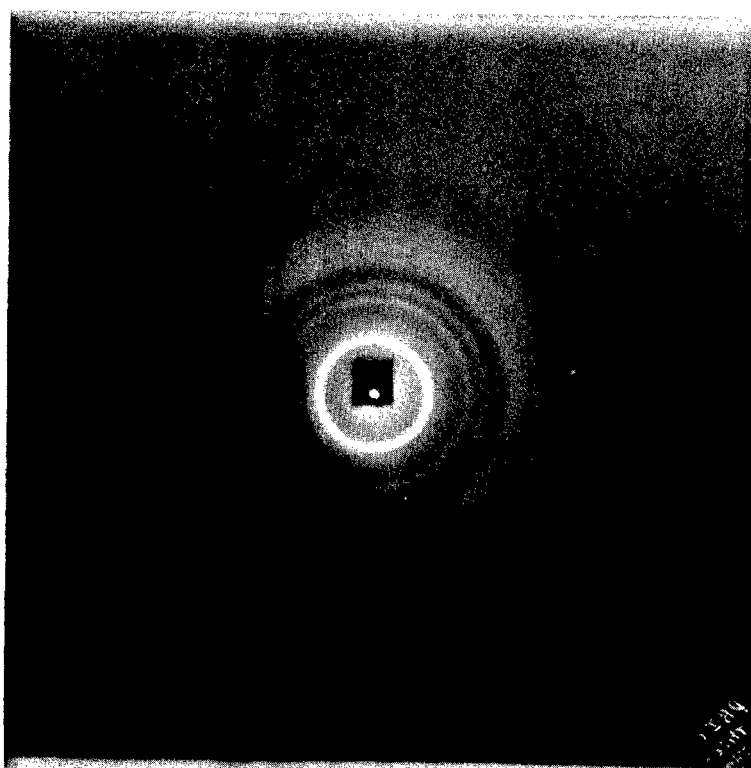


Fig. 34  
Thick Film of PBIC

Table III

Observed Bragg's Spacings for Ultra-thin  
and Thick Films of PBIC

<u>Ultra-thin Film</u>	<u>Thick Film</u>
11.37	11.74
	7.31
6.93	5.89
4.85	4.91
4.10	4.55
3.86	4.15
	3.79
3.07	3.40
2.84	3.07
2.50	2.84
	2.57
2.29	



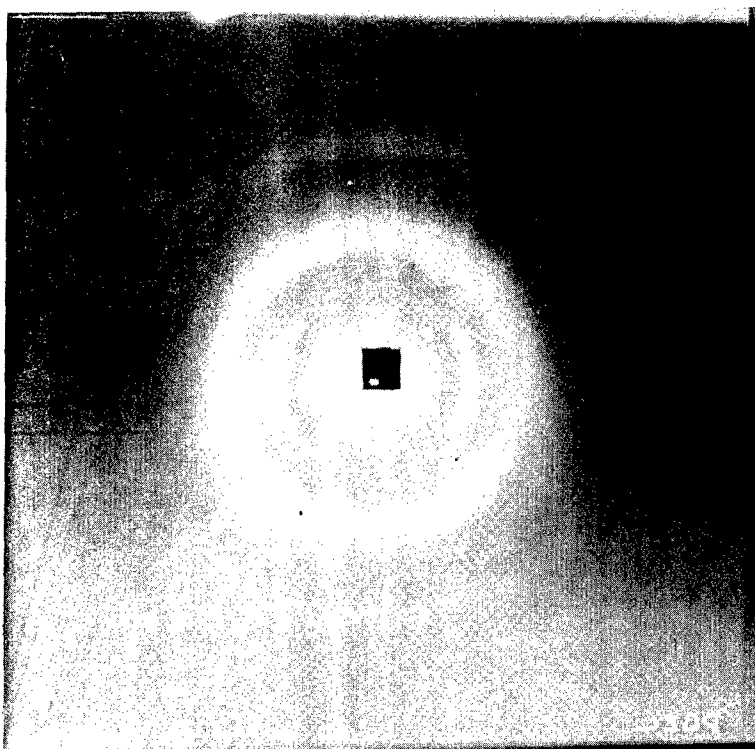


Fig. 35  
PBIC Fiber Pattern (Fiber Axis Vertical)

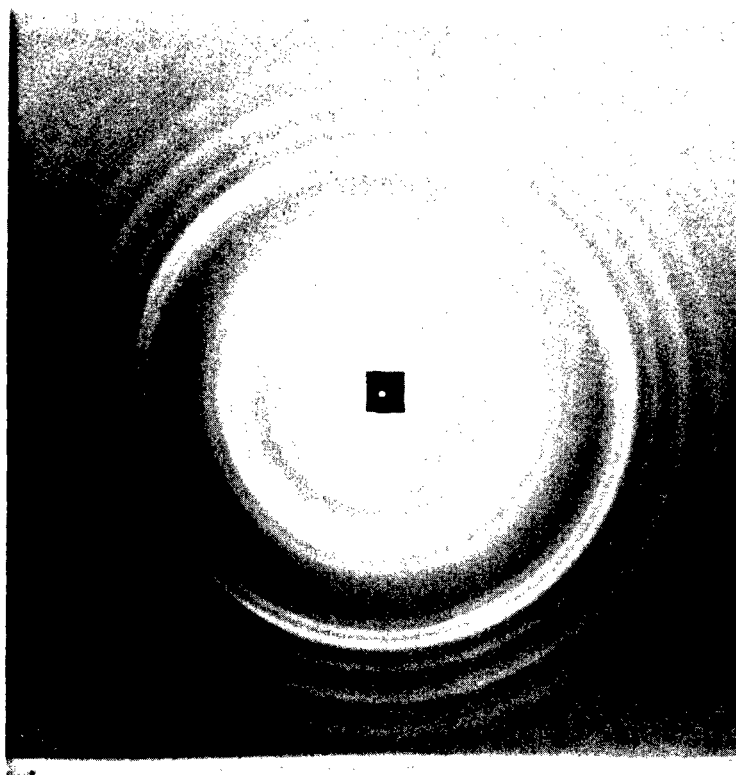


Fig. 36  
PBIC Gel Precipitated From Polymerization



Fig. 37  
Electron Diffraction of PBIC

Table IV

Observed Bragg's Spacings for Poly(n-butyl Isocyanate), Å

<u>Oriented Sample</u>	<u>Unoriented Sample</u>
20.52 (E) *	10.94
10.31 (E)	4.85
	4.29
7.22 (E)	3.94
	3.02
6.55 (E)	2.98
	2.86
4.85 (M)	2.68
	2.46
4.29 (M)	2.31
	2.03
3.02 (M)	1.89

\* E: Equatorial

M: Meridional

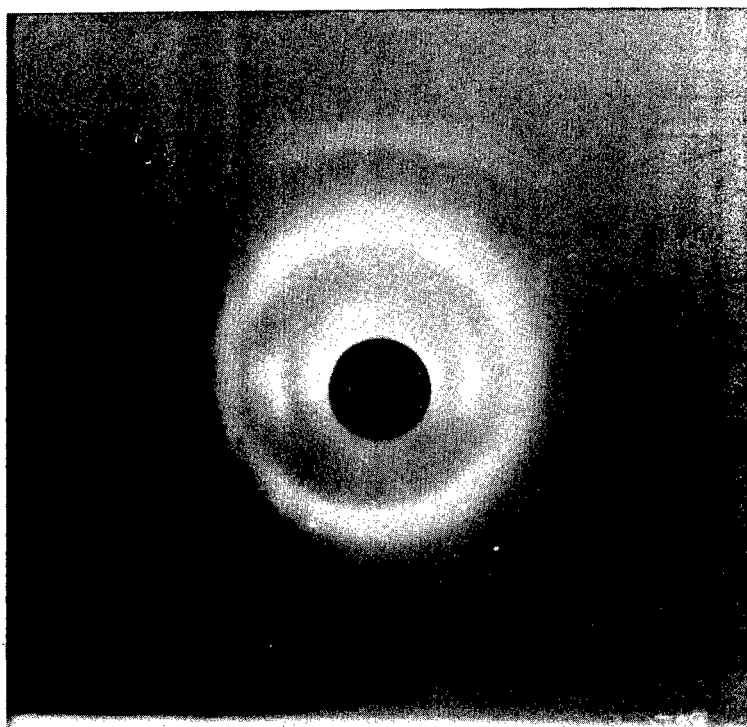


Fig. 38

Fiber Pattern of POIC

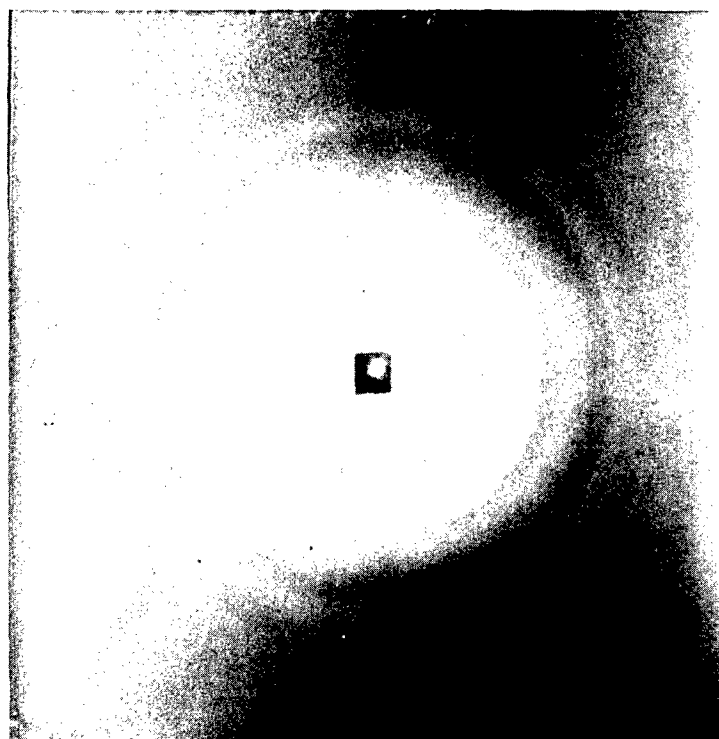


Fig. 39  
POIC Gel ppt From Polymerization

Table V

Observed Bragg's Spacings for Poly(n-Octyl Isocyanate),  $\text{\AA}$

Oriented Sample

19.33 (E)  
16.44 (E)  
14.32 (E)  
10.94 (E)  
10.31 (E)  
7.22 (E)  
6.25 (E)  
6.19 (E)  
4.85 (M)  
  
4.29 (M)  
3.02 (M)  
2.93 (M)

Unoriented Sample

19.33  
16.44  
  
10.94  
  
7.22  
6.25  
  
4.85  
4.55  
4.29  
3.02  
2.93  
2.57

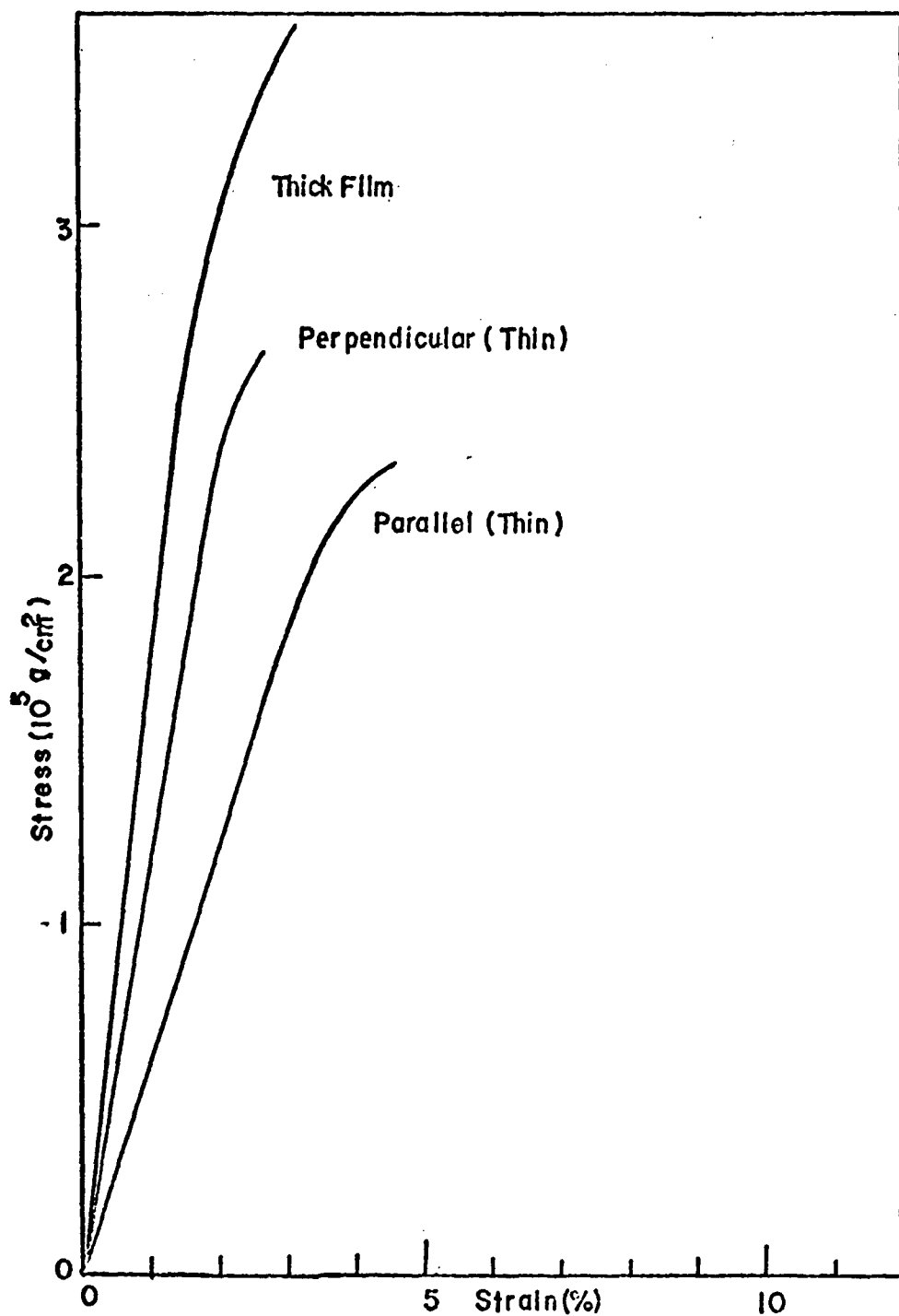


Fig .40. Stress-Strain Curves of  
Polystyrene (260,000 Mw ) Films



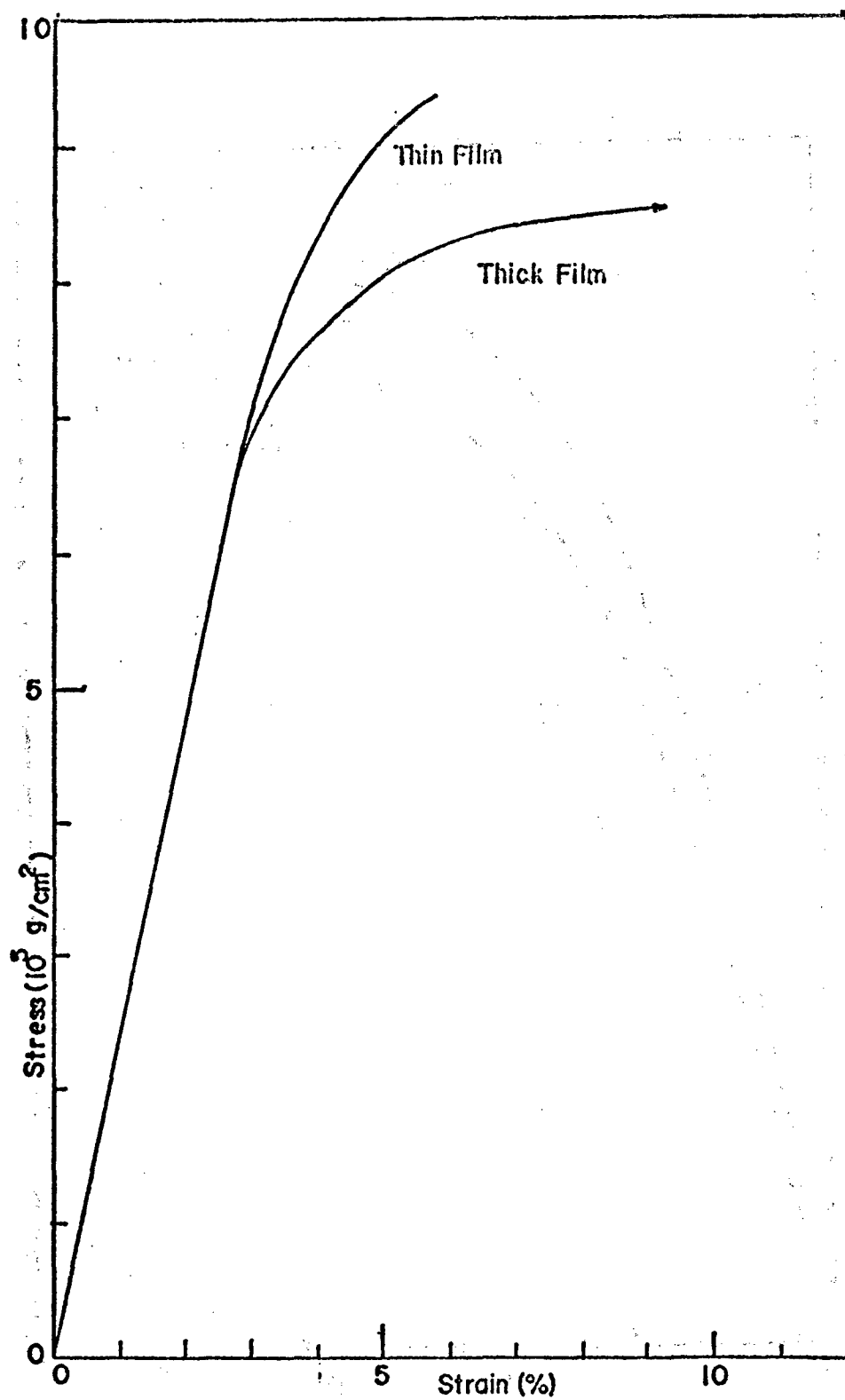


Fig. 41. Stress-Strain Curves of Cellulose Acetate Films

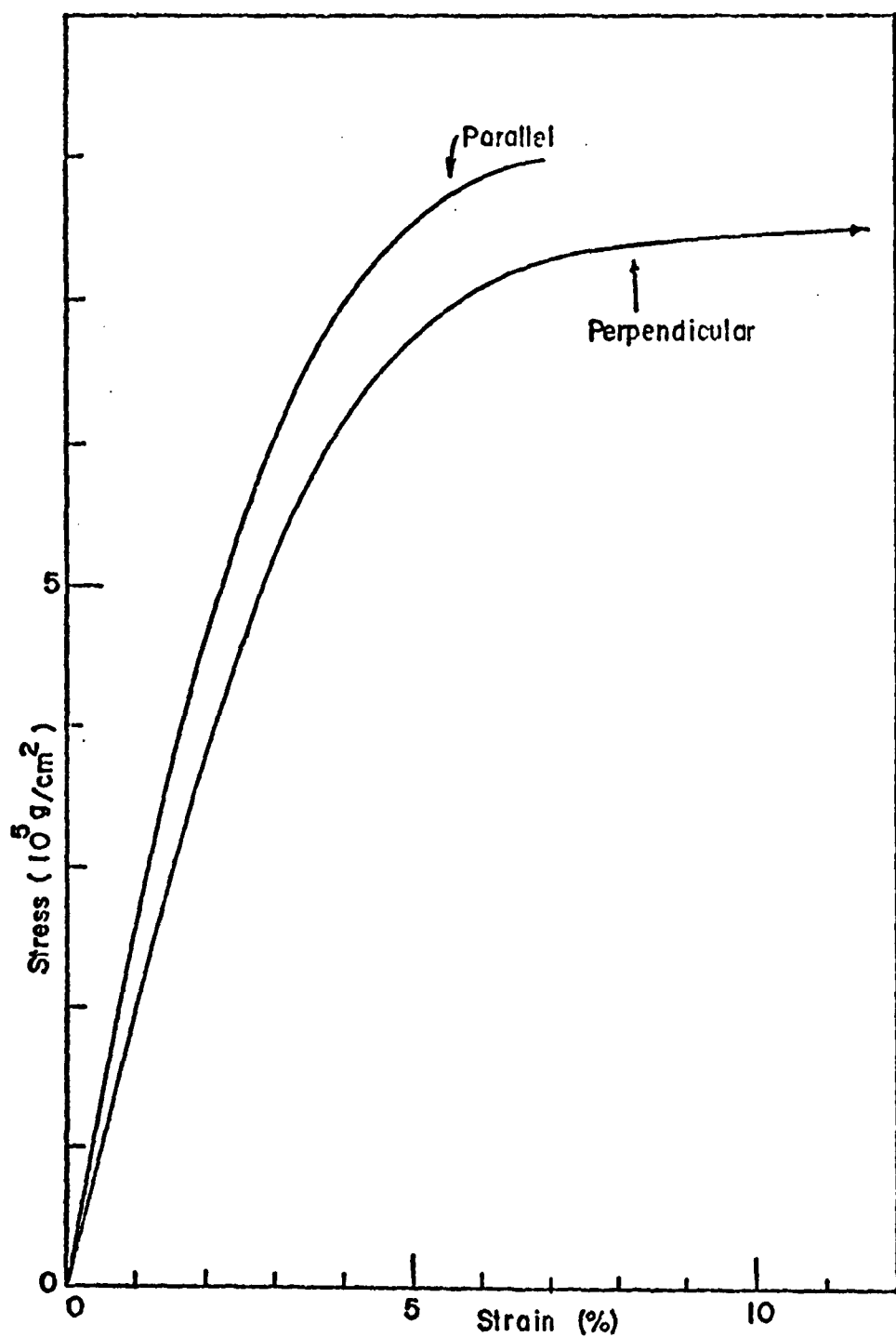


Fig. 42. Stress-Strain Curves of  
Cellulose Acetate Thin Films